CHARACTERISATION OF NETWORK STRUCTURE IN RECYCLED RUBBER

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Abstract

Produced by existing size reduction technologies, rubber crumb is the most valuable type of recycled material. However, only a limited amount of untreated crumb can be used in new tyres due to significant property loss. The *de-vulcanisation process* offers the potential for providing high quality recycled material that can be used as a substitute for virgin rubber. Rubber materials produced during industrial trials that formed the development stages of the novel *DeVulCO"2 de-vulcanisation technology*, were used in this work.

A practical way to characterise de-vulcanised and re-vulcanised waste tyre materials and blends with virgin compound was established. This work showed that simple to obtain and understand parameters, acquired from tests that are commonly used in the rubber industry, such as Mooney viscosity, Mooney relaxation and curing can be successfully used to indicate the efficiency of the de-vulcanisation process and hence, to assist the research and development stages of the de-vulcanisation process and to assure quality control. Good correlation was evident between these parameters and the network characterisation parameter (V_r) obtained from the swelling measurements that are known to be a reliable guide but are more time consuming to perform. In this work, the Mooney relaxation test was successfully extended to characterise some *de-vulcanised* compounds (automotive weather strip and clothing tape).

In addition, the swollen-state ^{1}H-NMR technique was successfully applied to characterise *de-vulcanised and* subsequently *re-vulcanised* "closed-loop" tyre materials. A new tool to measure the efficiency of the de-vulcanisation process has been devised, based on a comparison of the peak areas in the olefinic region of rubber extracts analysed by the liquid ^{1}H-NMR technique. This technique is capable of characterising different components of a rubber blend (e.g. NR, BR) and is suitable for carbon black filled compounds.

The results of this work have confirmed the potential of the *DeVulCO"2 technology* and have indicated that up to 20% of de-vulcanisate can be blended with virgin tyre compound without significant deterioration of the key performance properties.

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Contents

List of Principal symbols

MV	Mooney Viscosity
α	Rate of Stress Relaxation
(α+1)	Mooney Elasticity Parameter
k	Constant (Mooney Relaxation torque at 1second after the rotor is stopped)
$M_{ret.30s}$	Percent Mooney Torque retained at 30 seconds after the rotor is stopped
D_{20},D_{90}	Mooney Relaxation Parameters
M_H	Maximum Rheometer Torque
M_L	Minimum Rheometer Torque
M_{90}	Rheometer Torque at 90% cross-linking
t_{90}	Time to 90% cross-linking
t_{s2}	Scorch Time
I	Cure rate index
V_r	Volume Fraction of Rubber in Swollen Vulcanisate
V_s	Molar volume of solvent
p	Density
χ	Polymer-solvent Interaction Parameter
Ƞ	Solubility Parameter
η_{phys}	Physically Effective Cross-link Density of rubber
$\bar{M}_c$	Average Molecular Mass between cross-links
m	Sample weight
T_g	Glass Transition Temperature
E	Weight fraction of acetone extractable material
H%	Peak Width Parameter (NMR)

List of Abbreviations

ATR	Attenuated Total Reflectance
BIIR	Bromo-Isobutylene-Isoprene Rubber (Bromo-Butyl Rubber)
BR	Butadiene Rubber
CBS	N-cyclohexylbenzothiazole-2-sulphenamide
CRD	Cross-Link Density
CR	Chloroprene Rubber
DEG	Diethylene Glycol
DRT	De-vulcanised Rubber Tyre
DTDM	4,4-Dithio dimorpholine
DOTG	Di-o-tolylguanidine
DPG	Diphenyl Guanidine
DSC	Differential Scanning Calorimetry
ELT	End-of-Life Tyres
ENR	Epoxidised Natural Rubber
EPDM	Ethylene-Propylene-Diene Monomer
ETRMA	European Tyre and Rubber Manufacturers' Association
FTIR	Fourier Transform Infrared
GRT	Ground Rubber Tyre
IR	PolyIsoprene Rubber
IIR	Isobutylene-Isoprene Rubber (Butyl Rubber)
MBS	N-morpholylbenzothiazole-2-sulphenamide
MBT	2-Mercaptobenzothiazole
MBTS	Dibenzothiazol-2-yl Disulphide
MU	Mooney Units
NR	Natural Rubber

NBR	Acrylonitrile-Butadiene Rubber (Nitrile Rubber)
NMR	Nuclear Magnetic Resonance
ODR	Oscillating Disc Rheometer
PP	Poly(Propylene)
Pphr	Parts Per Hundred Rubber
RF	Radio Frequencies
RT	Relaxation Torque
RMA	Retread Manufactures Association
$scCO_2$	Supercritical Carbon Dioxide
SBR	Styrene-Butadiene Rubber
TGA	Thermogravimetric Analysis
TBBS	N-tert-butylbenzothiazole-2- sulphenamide
TMS	Tetramethylsilane
TMTD	Tetramethylthiuram Disulphide
TPE	Thermoplastic Elastomer
UNEP	United Nations Environment Programme
WRAP	Waste and Resources Action Programme
ZDBC	Zinc Dibutyldithiocarbamate
ZDEC	Zinc Diethyldithiocarbamate
ZDMC	Zinc Dimethyldithiocarbamate
ZnO	Zinc Oxide

Chapter 1: Introduction

The best way of recycling waste tyres is to reduce them to rubber crumb. However, only a very limited amount of untreated crumb can be used in new tyres without affecting their properties and performance. The *de-vulcanisation process* offers the potential for providing high quality recycled material that can be used as a substitute for virgin rubber. The problem for manufacturers is to know how much of it can be safely used.

Rubber materials have an optimum cross-link density range for practical use. Although characterisation of re-vulcanised rubber can be done by a number of established techniques, up till now characterisation of de-vulcanised tyre crumb has presented a significant problem as it has been either challenging (e.g. swelling) or impossible (e.g. stress-strain measurements).

Hence, the main aims of this work are:

- To characterise network structure of de-vulcanised and re-vulcanised closed-loop tyre materials produced during industrial trials by the *DeVulCO"2* technology.
- To develop a practical and reliable technique to evaluate the effectiveness of the de-vulcanisation process during Research & Development and ultimately for quality control.

This study has adopted the following objectives to achieve these aims:

- To review existing and emerging tyre waste utilisation techniques in order to identify the most promising and environmentally friendly recycling method available for commercialisation
- To review existing and emerging network characterisation techniques and to evaluate their potential to characterise de-vulcanised and re-vulcanised rubber compounds
- To show that the recycling method used in this work is effective and competitive
- To evaluate possible correlations between relevant rubber network characterisation parameters and mechanical properties

Internationally approved, traditional and emerging waste management utilisation techniques for used and waste tyres (e.g. re-use, re-treading, pyrolysis and incineration, recycling and de-vulcanisation) have been reviewed in Chapter 2. This review identified recycling of whole tyres and tyre buffings as the main acceptable utilisation technique for tyre waste. Produced by existing size reduction technologies, rubber crumb is the most valuable type of recycled material. However, only a limited amount of untreated crumb can be used in new tyres without causing significant property loss. The recycled material is effectively acting only as a filler hence, modification of the crumb to improve its ability to be incorporated into the new rubber matrix would be desirable. This can be achieved through surface modification and de-vulcanisation. The de-vulcanisation process is based on a selective break up of cross-links in vulcanised rubber and offers the highest quality recycled material that can be used as a substitute for virgin rubber. A detailed review of well-established and emerging de-vulcanisation techniques, carried out in section 2.5 of Chapter 2,

identified *mechano-chemical DeVulCO"2 technology* as the most promising and environmentally sound rubber recovery method (proven on a laboratory scale and ready for commercialisation) with great potential for developing high end applications, including new tyres. The attraction of this technique is that it can be adapted (e.g. equipment configuration, processing conditions, chemicals) to address variations in recycled rubber composition, hence it can offer a "tailored" de-vulcanisation process.

To optimise the process development, compound development and product development stages of any de-vulcanisation process, a practical, effective and reliable characterisation technique is required to characterise the materials produced. A comprehensive review of the existing and emerging characterisation techniques and their usefulness for characterising de-vulcanised rubber materials has been presented in Chapter 3.

The Mooney viscosity test was identified (section 3.2) as a useful indicative technique for the characterisation of de-vulcanised rubber material. As the Mooney viscosity value relates to the modulus, the removal of cross-links during de-vulcanisation leads to reduction in modulus and the viscosity value. However, the value of viscosity can also be influenced by changes in the material's composition (e.g. additives) and processing conditions. This review highlighted that the use of other Mooney viscosity measurements, including Mooney torque relaxation data (not currently applied in de-vulcanisation studies) can provide valuable information on elasticity, leading to a more accurate evaluation of the de-vulcanisation process.

This review also outlined (section 3.3) a successful application of equilibrium swelling measurements to characterise the network structure of unfilled rubber. However, when applied to blends and/or filled compounds, such as tyres, this technique can lead to significant errors, particularly in the determination of the cross-link density parameter. Different approaches for calculating the cross-link density parameter of filled rubbers have been reviewed and showed the lack of information available (e.g clear assumptions and definitions) to validate and compare the results.

The usefulness of spectroscopic techniques has been evaluated in section 3.6. The FTIR technique has mainly been used in de-vulcanisation studies to make comparison between the chemical composition of de-vulcanised, re-vulcanised and virgin rubbers. This review identified the *swollen state* ^{1}*H-NMR* technique as the most suitable and effective tool for network characterisation of carbon black filled rubber blends and hence, showed strong potential for characterising the recycled tyre waste materials used in this study.

The rubber materials used in this research work were generated during industrial trials from the development stages of the new *DeVulCO"2 de-vulcanisation technology*. Waste rubber obtained from different sources of the same type of product, can make it difficult to accurately evaluate de-vulcanised material. This was certainly the case with tyre waste crumb that originated from more than one source. To eliminate this inconsistency a truck tyre tread material of known formulation

was subjected to a typical tyre re-treading process to produce rubber crumb for the de-vulcanisation process. After being de-vulcanised by the *DeVulCO"2* process, the crumb was then blended with virgin material to produce the "closed-loop blends" that formed the central part of the investigation for this research work. A full explanation of the materials used in this work and details of the experimental procedures employed for their characterisation are outlined in Chapter 4.

The results of the practical work are presented and discussed in Chapter 5. Finally, important conclusions drawn from the present work along with some recommendations for further work are included in Chapter 6 and Chapter 7 respectively.

Chapter 2: Literature review - Tyre waste utilisation techniques

Introduction

Rubber's unique properties are attained during sulphur vulcanisation when crosslinks are created between the molecular chains. These crosslinks cause problems with recycling as they are very difficult to remove without breaking the main polymer chain and significantly degrading the rubber, in contrast to thermoplastics which can be easily reshaped on heating. This fundamental difficulty is the underlying reason for the vast amount of rubber waste that presents such a serious environmental problem for the UK and worldwide.

A significant proportion of the mountain of rubber waste comes from discarded tyres as approximately seventy percent of all natural and synthetic rubbers go into tyre production [1]. It is estimated that between 1.4 and 1.5 billion new tyres are produced worldwide each year [2] and this figure is predicted to increase further over the next 15 years due to rapid industrial developments in China and India [3–5]. In addition, a report published by the World Business Council for Sustainable Development (WBCSD) emphasises that around 1 billion end-of-life tyres (ELT) were generated worldwide in 2008 on top of 4 billion ELT already held in stockpiles and landfills [2].

Tyres are not biodegradable and, if they are not responsibly disposed, can present serious health and environmental risks by creating ideal homes for rodents and breeding sites for mosquitoes, responsible for dengue and yellow fever. Waste tyres also contribute to air and water pollution due to uncontrolled fires, lead to leaching of chemicals and present problems associated with ecotoxicity. These concerns have been well documented and addressed in current policies, legislations and regulatory documents, concerned with tyre recycling [6–8].

However, waste management systems and as a result, their efficiency vary greatly from one country to another. Within Europe (EU Member States) alone there are, three different ELT management systems in operation in:

- Producer responsibility system (Belgium, Estonia, Finland, France, Greece, Hungary, Italy, the Netherlands, Norway, Poland, Portugal, Romania, Slovenia, Spain, Sweden and Turkey)
- Free market system (Austria, Bulgaria, Croatia, Germany, Ireland, Switzerland, UK)
- Tax system (Denmark, Slovak Republic)

The most popular is the Producer responsibility system, where the law defines the legal framework and assigns waste management responsibilities to the tyre production companies. The next most popular, the Free market system, employs legislation with set objectives but does not specify who is responsible for their delivery. The UK operates under the "managed free market" system where the tyre collectors have responsibility for reporting to national authorities. The least popular is the Tax system (currently operating in two European countries) which places waste management responsibilities of ELT on the State with the producer paying a tax for the service.

According to a report [8] produced by the European Tyre and Rubber Manufacturers' Association (ETRMA), the Producer responsibility system is "the most suitable, robust and sustainable" in dealing with waste & ELT tyres to achieve both a high recovery rate and in developing applications with "added value" through full use of the properties of rubber. The system implicitly encourages development of high performance applications, including new tyres. Hence, it is encouraging that this system has been identified as a good example for adoption by a wider cohort of European countries.

Taking into account that the majority of emerging technologies, capable of producing high quality recycled material suitable for high performance applications, are still expensive and (or) only proven to work on a laboratory scale, some of the traditional techniques which have become unacceptable (e.g. landfill, stockpiles, illegal dumping and export) are still the preferred choice of disposal [9,10]. Hence, there is a great need to develop commercially viable and efficient recycling technologies to deal with used and waste tyres.

The United Nations Environment Programme (UNEP) Basel Convention International technical guidelines document [6] considers the following approved traditional and emerging management utilisation techniques for used and waste tyres:

- Re-use
- Re-treading
- Pyrolysis and incineration
- Recycling
- De-vulcanisation

This review has provided an overview of these waste utilisation techniques and highlighted their advantages and limitations and evaluated their potential for dealing with the ever increasing amount of used and ELT. The most promising method (capable of turning waste material into high quality recycled material suitable for high performance applications) has been identified and studied in more detail and has formed the base of this research project.

2.1 Re-use

The term "re-use" has a number of meanings in the literature and can vary from the extension of product life to the use of the product in new applications. Figure 1 shows the hierarchy of waste utilisation. As a waste disposal method, re-use is the preferred choice after the waste minimisation method. Tyres are an essential component to road and air transport and until an alternative is invented, prevention is not feasible and minimisation of use is not relevant to this work.

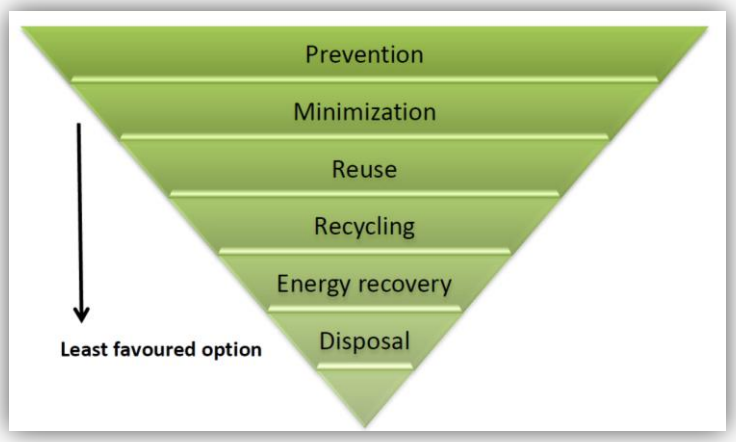


Fig. 1 Used and waste tyre management hierarchy [6]

Re-use: direct re-use/export

A part-worn tyre can be defined as a tyre that has been subjected to any use or wear but has not reached the end of its useful life and does not require any treatment for further use. These tyres are re-usable in Europe as a second hand purchase. Part-worn tyres are also exported to non-European countries. However, these tyres will reach a point where they become so worn out that they cannot continue to be used legally and will have to be considered for re-treading or contribute to the ELT [11].

Fig. 2 is based on the data [5] (Statistics report) published by the ETRMA and shows that a relatively small percentage (around 10%) of all used tyres in 2012 were re-used/exported. It is interesting to note that this value has only fluctuated slightly (±2%) over the period between 1994 and 2012 (Fig. 3) and this value (10%) is predicted to stay fairly constant in the near future [12].

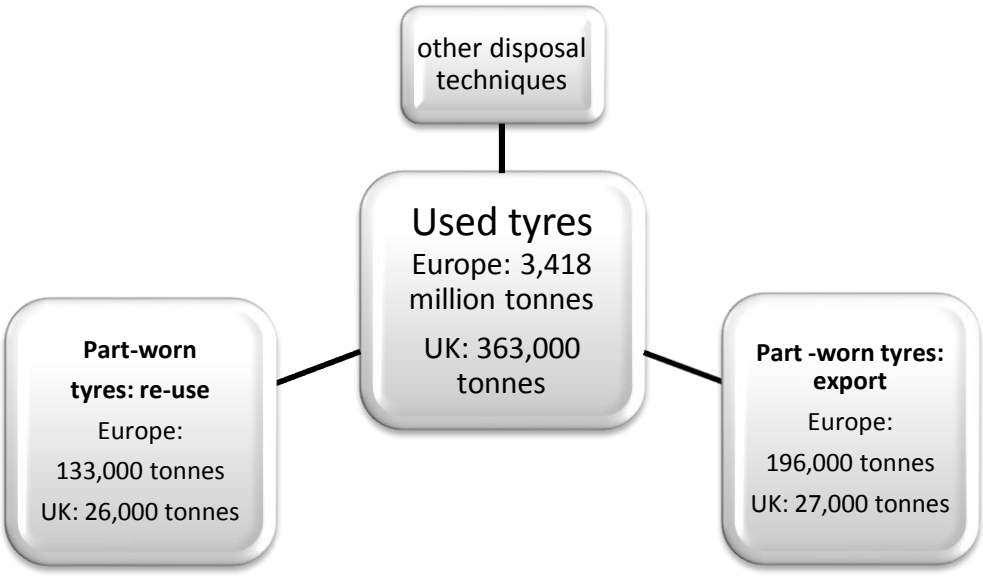


Fig. 2 European and UK data [5] on Re-use & Export of part-worn tyres in 2012

The reason for this is the tight safety legislation operating in Europe to control the legal limit of the tyre tread depth and tightening of legislation in non-European countries.

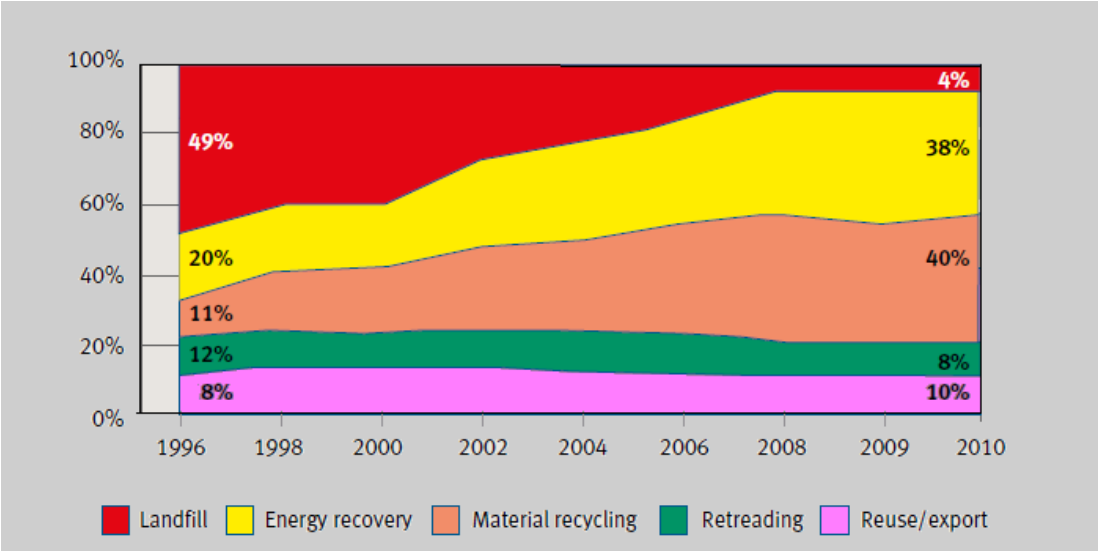


Fig. 3 Evolution of recovery routes in Europe [8]

Re-use: whole tyres/ tyre bales

As illustrated in Fig.3, the percentage of tyres sent to landfill in Europe has sharply declined between 1996 and 2008 following the Directive on the Landfill of Waste (1999/31/EC) that banned burying whole tyres from 2003 and shredded tyres from 2006. This led to development of alternative applications for the whole ELT tyres, particularly in landfill engineering, civil engineering and construction [13,14]. ELT can be compressed into tyre bales of specified dimensions and characteristics and have proved to be successful in a number of applications: for example for flood control, mud and erosion control, soil elevation, impact and as sound barriers for motorways and racetracks, shock absorption for foundation walls and other similar applications. However, it has been predicted that landfill engineering application are going to decline with time [12] due to general negative perception of landfilling and problems associated with it [6–8] and progress in developing more effective and sustainably sound waste minimisation techniques. On the other hand, the use of baled tyres in civil engineering and construction in the UK is likely to increase due to standardisation of bales [15] introduced in 2010, their affordable cost [9] (£10 to £31 per tyre bale) and their waste minimisation/material saving advantage over traditional construction aggregates.

Re-use: shredded tyres

Another way of re-using ELT is to size reduce and recycle them as a material in new applications. Whole tyres can be mechanically sheared into shreds (20mm - 400mm), chips (10mm - 50mm) and granules (0.8mm - 20mm) These size-reduced materials can be re-used in a number of civil engineering and construction applications [16,17]. They are also an essential preliminary to making rubber crumb (0.07mm - 1.4 mm). In order to minimise the cost of transporting whole tyres, shredding often takes place near disposal sites and many shredders are portable. But tyres are

high performance engineering products designed to be resistant to cutting and tearing. Hence, cutting equipment is relatively expensive to maintain because of the abrasiveness of the rubber and reinforcing material (steel and textile used for this purpose are not typically removed prior to shredding). In addition, the process also requires a large energy input.

Re-use: tyre crumb

Tyre crumb has become a valuable source of material that can be mainly used in three types of applications [18] :

- without any treatment (consumer and civil engineering applications: artificial turf fields, playgrounds, asphalt, etc)
- surface modified to improve its compatibility with the main matrix component (as a substitute for virgin material, TPE (thermo-plastic elastomer), concrete
- reclaimed/de-vulcanised and used as a substitute for virgin material (substitute virgin material in high performance applications, including tyres)

Rubber crumb can be obtained by different techniques that have been overviewed in section 2.4 of this work under *size reduction technology*. The size of the crumb varies from fine (below 0.07 mm) to course (0.5mm – 1.4mm).

To summarise, re-use does have the potential to be increased through the tyre bailing process used in flood defence schemes and construction applications. However, flood defence schemes are unlikely to offer a sufficiently large volume markets in themselves. The use of material in construction is still limited due to strict building specification requirements. Hence, there is a limit to the amount of opportunities for re-use of whole and baled tyres. However, rubber crumb has great potential for recycling as the primary ingredient for new de-vulcanisation and surface activation technologies. This leads to an extension of the possible applications for which it can be used and includes high value application as a whole, or as a partial substitute for virgin material.

2.2 Re-treading and Re-Use

Re-treading is a well-established re-manufacturing technique that aims to extend the life of worn tyres by replacing the old tread (where the tread depth is below the legal limit) with a new tread and is the most favoured option of waste disposal after re-use (Fig.1).

The use of re-treaded tyres began in the 1920's. This waste management method is environmentally friendly as it helps to reduce demand for natural resources and energy by between 65% to 70% every time an old tyre is re-treaded and re-used, instead of making a new one [19]. Case studies on the costs and benefits of re-treading were published by WRAP and identified that on average a re-treaded tyre is 10% cheaper than a new budget tyre [20]. The UK based Retread Manufactures Association (RMA) indicates [9] that the cost and demand for re-treaded tyre depends on a number of factors: for example the number of re-treading companies in the area, the cost of a new tyre and the availability of cheaper imported tyres.

Although all types of tyres can be re-treaded, truck tyres are particularly attractive for this purpose as they are designed to be re-treaded 4 to 5 times. Re-treading of car tyres appears to be less popular due to the economics of re-treading car tyres and the public's perception regarding the safety of their use [12].

Based on the ETRMA report [5] 324,000 tonnes of used tyres in Europe (28,000 tonnes in the UK) were re-treaded in 2012. This indicates that only around 9% of all waste tyres in Europe were managed through the re-treading process. As illustrated in Fig. 3, 12% of all used tyres were re-treaded in 1996 with the figure staying fairly constant until 2008 when it dropped to 8%. This figure increased by 1% between 2010 and 2012 and is predicted to stay constant for the near future. However, the ratio between the number of truck tyres and car tyres subjected to re-treading is going to increase further [12], as it has been established [9] that removing rubber from a truck tyre requires less effort and provides a higher content of natural rubber than from a car tyre. The old tread is usually subjected to a size reduction recycling process (e.g shredding, grinding) and is commonly used as cheap filler with a very low inclusion rate (up to 5%) [19,21–23]. However, if de-vulcanised, the material has the potential to be recycled and re-used in higher performance applications, including new tyres and re-treads at much higher inclusion rates.

To sum up, re-treading is a well- established technique that has generating a steady demand for part worn tyres over the last thirty years. This demand depends on the cost of new tyres (cost of virgin material and energy cost) and the availability of cheaper imported tyres. The overall demand for re-treading is predicted to stay constant, however with an increase in truck tyres and decrease in car tyres. Emerging de-vulcanisation technologies can also contribute to an increase in the re-treading market, particularly among truck tyres, driven by the cost of virgin material.

2.3 Pyrolysis and incineration

Incineration is restricted to the use of whole or shredded tyres as a tyre- derived fuel (TDF) in the manufacture of Portland cement. Due to their high calorific value (33 $MJkg^{-1}$), ELT can also be used as a substitute for coal or to provide an energy source to generate electricity in the pulp and paper industry. However, the barriers [24] for wider use of ELT as a substitute for coal, natural gas or oil are the unreliability of tyre supply, the need for substantial investment to install new feed systems capable of accepting ELT, the increased costs associated with meeting strict emission standards and the negative public perception towards the burning process.

A statistics report [5] published by the ETRMA, shows that although the energy recovery process in Europe has grown from 11% in 1996 to 37% in 2012 it is still currently restricted to the use of ELT in cement kilns (91%) with a small amount being used by power plants or co-incinerated with other waste (9%).

Emerging opportunities

Pyrolysis is a process in which the chemical bonds in rubber are completely broken by application of heat in an air free environment to chemically breakdown the material into its components without causing combustion. At temperatures below 400ºC the major pyrolysis product is carbon char and

at higher temperature (500 ºC - 900ºC) more liquids, oils and gases are produced. Vacuum pyrolysis has been successfully trialled to break down ELT to yield valuable components such as oil, gas, fibreglass, steel and carbon black [24].

Carbon black obtained via pyrolysis (pyrolytic carbon black) tends to be more expensive, varies in quality and has less reinforcing power than its original constituent, produced from petroleum oil and hence, its applications are limited to a feedstock for the production of activated carbon or as a reinforcement in bitumen and some plastics [24]. A number of studies [25–27] investigated and reported the use of pyrolytic carbon black as a filler in rubbers, including ethylene-propylene-diene rubber (EPDM) and styrene-butadiene rubber (SBR), comparing its processability and reinforcing characteristics to the lower grades of commercial carbon black. However, to generate real demand, pyrolytic carbon black would have to be produced on a commercial scale with a consistent structure and hence, properties.

Pyrolytic oil has a high calorific value [24] (around 44 MJ kg^{-1} compared to 33 MJ kg^{-1} of heating value of ELT) and can be used directly as a fuel (after preliminary treatments) or subjected to distillation. When subjected to distillation, the lighter fractions can be used to produce valuable chemicals and as an extender oil in rubber formulations. Heavier fractions can be used in road bitumen. Investigations by Cataldo [28], revealed a potential use of heavy fraction of pyrolytic oil from ELT as a substitute to petrolium derived oil as a plastisizer in NR compounds.

The gases obtained via pyrolysis are rich in hydrogen, methane, propane and butane fractions and have a high calorific value (46 MJ kg^{-1}) that also make them an attractive fuel.

Despite extensive work to develop applications for pyrolytic by-products, success is hampered by the high cost of initial plant investment and hence, the high production volumes that would be necessary to make the process commercially viable. As an example, the UK based PyReco company has already invested £1 million of government funding and would require an additional £80 million to commercialise their pyrolysis processing plant to produce oil, gas and high quality carbon black from ELT. To be economically viable, the plant would have to process a minimum of 200 tonnes of shredded tyres every 24 hours [29]. This is not a practical volume for a host of reasons (e.g. transportation, availability, local environmental concerns, etc)

Therefore, energy recovery is currently restricted to the use of ELT in cement kilns and is predicted[12] to increase due to increased costs of fossil fuels. The use of waste tyres in cement kilns is a cheaper and more environmentally friendly substitute. However, when used as a fuel, ELT waste only recovers about 2% of the original compound cost [30]. Although the amount of ELT utilised through energy recovery in Europe is still relatively high (37% in 2012), it dropped by 3% between 2009 and 2012.

Thus, pyrolysis has the potential to greatly increase the intrinsic value of tyre components recovered from ELT, however the high cost of plant investment is currently preventing commercial production.

2.4 Recycling

Material recovery by recycling in Europe has grown from 6% in 1996 to 39% in 2012, showing the strongest growth rate in comparison to other approved utilisation techniques, including energy recovery [5]. The *Used & waste tyre management hierarchy* diagram (Fig. 1) shows that recycling is the most accepted and environmentally sound waste management method after direct re-use. A comprehensive overview of rubber recycling carried out by Bandyopadhyay et al [1] highlighted that the majority of recycling work carried out over the last two decades was concerned with waste tyres as they are the main contributors to all rubber waste.

A tyre is a complex high performance product, engineered using valuable energy and material resources. The typical composition of a truck tyre crumb is shown below:

Table 1: Composition of recycled truck tyre crumb

Constituents of Recycled Rubber Crumb	**Crumb rubber, pphr (parts per hundred rubber), crumb size 40 mesh**
Natural Rubber	71
Styrene-butadiene Rubber	18
Butadiene Rubber	11
Carbon Black	47
Inorganic material, mainly zinc oxide (ZnO)	11
Extractables (accelerator residues, anti-degradants, process oils, etc.)	13

Table 1 shows that recycled tyres have a high proportion of natural rubber and this makes them a valuable resource with high potential for use in various applications. The challenge for recyclers is the wide variety of tyre composition and design.

According to Roy et al [24] "to re-cycle" means to put or pass through the cycle again for further treatment or in a different application. In the case of "tyre recycling" the further treatment is the application of size reduction technology to recover rubber in the form of shreds, granules or crumb that can be put through an additional regeneration process known as de-vulcanisation. The de-vulcanisation process aims to achieve the ultimate goal of "closed-loop recycling" where waste rubber is recycled for re-use as a substitute for virgin material in new tyres.

Rubber crumb is the most valuable type of recycled material and is produced by a grinding process. Ground recycled materials are classified in accordance with approved standards in respect to their feedstock and sieve analysis [18].

The value of the recycled crumb material depends on its composition and the type of grinding process used (leading to differences in size and surface area of recycled particles) [21]. Particle size

is reported to influence processing and mechanical properties, with smaller particles leading to improved performance [31]. The influence of the particle's morphology is more complex and largely depends on application [21].

Size reduction technology

The three major grinding processes for obtaining rubber crumb are ambient, cryogenic and wet grinding. These processes are well developed and documented in the literature [1,11,32]. The crumb produced by *ambient grinding* is relatively large (10-40 mesh) having particles of irregular shape with rough texture and high surface area. Additional grinding steps can reduce the particle size further (to 80 mesh). This process is carried out at ambient temperature but can generate a large amount of heat as the rubber is subjected to cutting, tearing and shearing and hence requires strict temperature control to protect rubber from thermal degradation. This process is readily commercially available and the majority of rubber crumb is obtained using this technique (Fig.4)

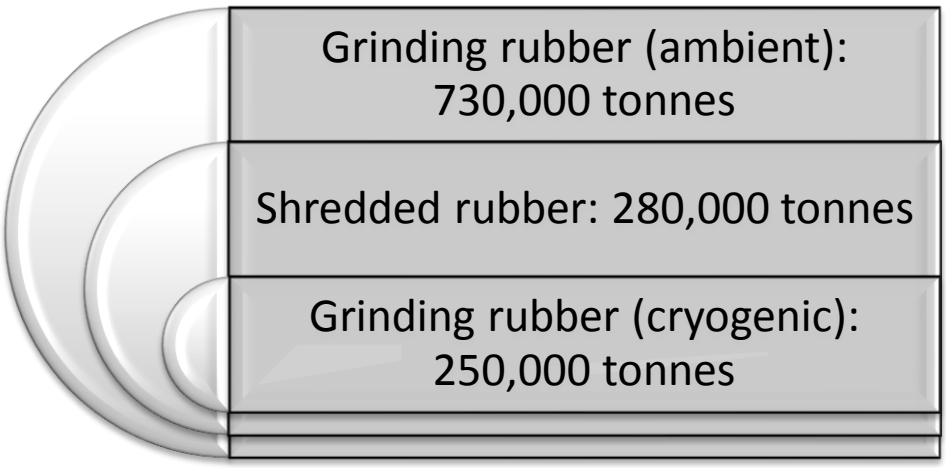


Fig. 4 Evaluation of size reduction processes in Europe in 2009 [6]

Wet grinding is a modified ambient grinding process that can be used when very fine-mesh rubber particles (60 to 120 mesh) are required. During this process, the rubber is continuously sprayed with water to prevent overheating.

Cryogenic grinding is used to obtain fine-mesh rubber particles (30-100 mesh) which are even and smooth in shape with a low surface area. This process requires liquid nitrogen (or another alternative medium) to freeze the rubber and is carried out below -80ºC. The size reduction is achieved through shattering and grinding of cryogenically embrittled rubber pieces with almost no heat produced, hence minimising thermal degradation. In addition, almost all of the fibre and steel are removed from the rubber (ambient grinding retains 0.5% of fibre and 0.1% of steel).

Lehigh Technologies Incorporation (Atlanta, US) has developed a commercial technique to produce ultrafine-mesh rubber particles from ELT [33]. Their product, "micromized rubber powder" or

MRD ranges in size from 80 to 300 mesh, produced by “cryogenic turbo mill technology”. The powder is suitable for a wide range of applications, including tyres.

The advantages of cryogenic grinding include high production volume and ease of fibre and metal separation. On the other hand, ambiently produced crumb from dry or wet process yields crumb with a higher surface area than cryogenic. A high surface area is associated with better adhesion to virgin rubber or to thermoplastics and leads to improved physical properties in the compounds. In addition, powder with higher surface area is reported to require a shorter mixing cycle during compounding and results in products with an enhanced appearance [24].

The ETRMA [5] have reported that over 1 million tonnes of recycled material in Europe were recovered in 2012 as shredded, granulated or crumbed material. Figure 5 shows that 12% of this material was used in civil engineering applications and 88% was used to make new, mostly low value products (e.g. car mats, wheels for dustbins & wheelbarrows, urban furniture).

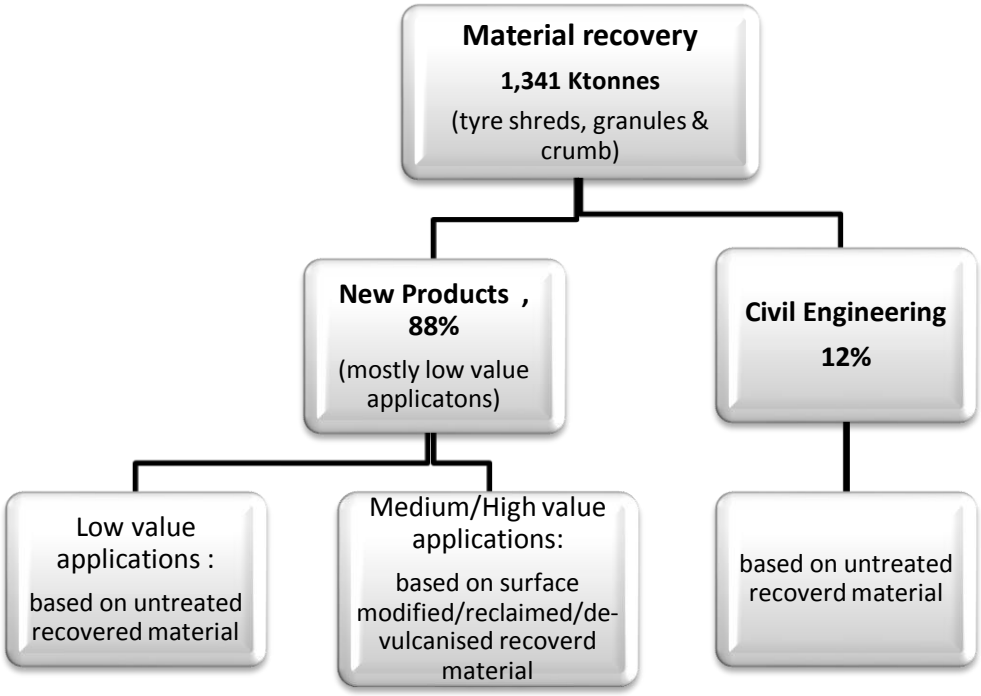


Fig. 5 Material Recovery Route of ELT in Europe in 2012

Untreated rubber crumb

These products were produced from untreated, size reduced materials. However, untreated material can only be used in limited quantities as it has an effect comparable to inert fillers. For example, shredded tyres are used as a filler to increase abrasion resistance and enhance the resilience in highway construction. However, only 10% to 20% of recycled material can be used for this purpose otherwise there is a detrimental effect on product quality. In general, the addition of

untreated rubber crumb to virgin material influences the processing behaviour of rubber compound and results in a 1% reduction of mechanical properties for every 1% of rubber crumb added [34]. Therefore, it has been reported [24] that the use of untreated rubber crumb in tyres should be restricted to 5%.

According to the overview of rubber recycling by Myhre et al [35], approximately 8 to 10% of recycled material was used in tyres in 2012. The main limitations were identified as restricted safety due to property loss and that better methods are needed for treating the rubber surface and regenerating the rubber through de-vulcanisation.

Treated rubber crumb

Surface treatment technology of rubber crumb has been overviewed by Bandyopadhyay et al [1,11] and include: surface coating, interfacial compatibilisation, high energy radiation, reactive gas treatment, chlorination, surface grafting, treatments with liquid rubber, treatment with trans-polyoctenamer and microbial treatment.

The surface treatment normally aims at improvement of the properties rather than improvement of the processing behaviour. The rubber crumb is surface coated with cross-linkable polymers containing vulcanising chemicals resulting in an increased reactivity toward chemical or physical bond formation with the polymer matrix in which it is embedded.

In conclusion, recycling is the main waste management method for ELT and is steadily growing. It is based on using size reduction technologies to recycle whole tyres and tyre buffings (by-product of tyre re-treading). However, applications for untreated recycled tyre material are limited to civil engineering and low value applications. Surface modification techniques can improve performance of rubber crumb and extend the application market but in general not more than 10% can be used as a substitute for virgin rubber. High value applications require de-vuclanisation.

2.5 De-vulcanisation

As highlighted by Myhre et al [35] de-vulcanisation offers the highest quality recycled material in terms of processing characteristics and mechanical properties. However, there are some obstacles that have to be overcome to place this process at the forefront of tyre waste management by material recovery. The main obstacles are reduced process safety (e.g. scorch time) and the need to use chemicals to assist the de-vulcanisation process.

De-vulcanisation is often considered under the heading of reclaiming technology as both processes aim to bring the rubber back to the" state" at which it can be mixed, processed and re-vulcanised. However, there is a distinct difference in *how* this aim is achieved within each technology.

Reclaiming is the oldest method for recycling used tyres. However, for a number of reasons (e.g quality of reclaim, environmental and health concerns about the chemicals used, the introduction of more complex tyre compositions and variable virgin material price) it has declined. The most used is the *digester reclaiming process* which starts with blending grinded rubber (less than 4 mm) with reclaiming agents and processing aids to soften and swell it. Heat is then applied to assist the

"digestion" process. Finally the "digested mass" is masticated using a two-roll mill or extruder to decrease the viscosity and break the vulcanised structure (cross-links as well as the main polymer chains). The process concludes with filtering (to remove any undigested material) and finishing processes. Rushton [36] has noted that the quality of the reclaimed tyre waste material can be improved by using rubber crumb of the same composition. However, not more than 5% of reclaim can be currently substituted for virgin material in production of new tyres.

De-vulcanisation of sulphur-cured rubber can be defined as the process of cleaving, totally or partially, poly-, di-, and mono-sulphidic cross-links (e.g. C-S and S-S) formed during the initial vulcanisation stage so that the de-vulcanised rubber can be re-vulcanised with or ideally without any additional additives [11,37–39]. Hence, de-vulcanisation is a selective process, that aims to "unzip" the cross-links only, without the break-up of the macromolecular chains. The aim of any de-vulcanised process is to achieve a full cleavage of the intermolecular bonds of the chemical network. However, some break-up of macromolecular chains does occur in practice. The main types of de-vulcanisation techniques are discussed below.

2.5.1 Mechanical de-vulcanisation

Mechanical de-vulcanisation is achieved through the repeated deformation of rubber particles under specific conditions of temperature and pressure. The main principle of the mechanical de-vulcanisation process is based on the difference in energy needed to break intermolecular bonds as compared to macromolecular bonds in vulcanised rubber: with S-S and C-S bonds requiring less energy to break than C-C bonds. In addition, the elastic constant of S-S bonds is relatively low, making them "stiffer" and more susceptible to break upon application of a shear force than C-S bonds and finally C-C bonds which are the most "flexible".

Table 2: Bond energies and elastic constants of C-C, C-S and S-S bonds[40]

Bond type	C-C	C-S	S-S
Bond energies, kJ mol^{-1}	370	310	270
Elastic constant, N m^{-1}	~ 100	Intermediate value	~ 3

A patented process of this type has been reported in the literature [32,39] where solvent swollen rubber (EPDM and CR) was forced through screens with decreasing mesh size at ambient temperature. It was claimed that the screens, made of metal alloys, acted as a catalyst to reduce the cross-link density of rubber. The mechanical properties were reported to decrease with small inclusions of de-vulcanised rubber into virgin compounds. Another mechanical process [41], implemented by Toyoda Gosei (TG) uses a "modular screw-type reactor" to manipulate and stress the rubber (NR and SBR) until it is de-vulcanised. The de-vulcanisation process is controlled by adjusting the screw configuration, rotational speed and processing temperature. Re-vulcanised

rubber material (EPDM) was blended with plastics (PP) to produce TPE. A mechanical method recently presented by Teixeira [42] is based on the well-known and commercialised *Watson B.HSM* de-vulcanisation technology but without the use of chemicals. The results presented were based on FKM (Fluoroelastomer) and EPDM rubbers. It was noted that although tyres can be potentially put through this process, their complex composition and contaminants (metal and fibre) may present a problem. The process is carried out in a high shear mixer (HSM) at low temperature (below 80º C) and schematically represented in Figure 6.

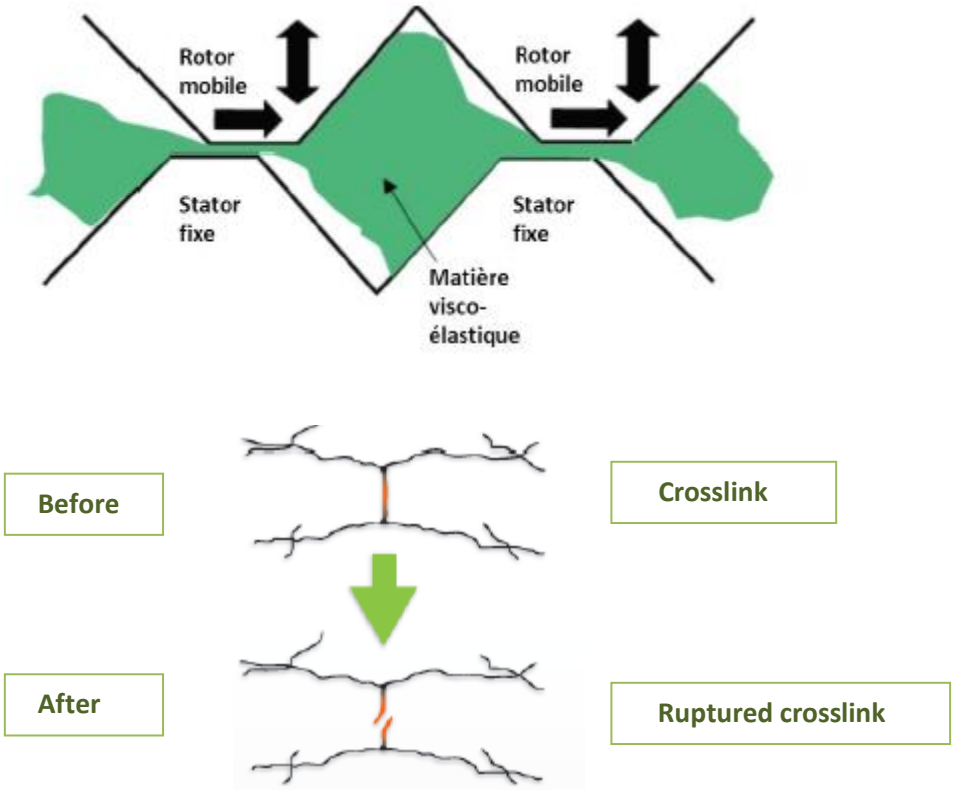


Fig. 6 Principle of the HSM de-vulcanisation process [42]

2.5.2 Chemical de-vulcanisation

The use of chemical probes for sulphur cured rubber was developed in the 1960s by the Tun Abdul Razak Research Centre (TARRC) known as the Natural Rubber Producers' Association. A chemical probe can be defined as "an analytical reagent which will react in some useful way with a specific network feature, which is capable of being homogeneously introduced into the network, and which can be easily extracted after the chemical reaction has been completed without side reactions". Chemical de-vulcanisation by probes and other chemical methods (catalysis, grafting, solution by o-dichlorobenzene) are well detailed by Warner [37].

The use of chemicals alone to effectively de-vulcanise a rubber network has not proved successful.

A combination of chemicals is often required to target different types of cross-links in sulphur cured rubbers, with the problem being that the most effective are carcinogenic or likely to present other health problems. However, chemical agents can be used for the surface treatment of rubber crumb to aid mechanical de-vulcanisation of rubber and to help study the rubber network [39].

2.5.3 Mechano-Chemical de-vulcanisation

Mechano-chemical de-vulcanisation is currently the most effective and commercially attractive method for de-vulcanisation of sulphur-cured rubbers, including tyres. A number of commercial technologies based on this technique are available and range from batch (e.g. De-Link, Levgum) to continuous (DeVulCO"2) process. The continuous de-vulcanisation process is particularly attractive as it offers de-vulcanised material of a consistent quality.

The principle of mechano-chemical de-vulcanisation is based on the selective breakup of chemical bonds through the application of shear, chemical agent(s) and often heat. Liquid CO_2 can be used as a carrier/swelling agent during extrusion. The process makes use of traditional rubber equipment (e.g. internal mixer, two-roll mill, extruder) in some cases with small modifications.

The chemical agents can be toxic and have to be carefully selected. WRAP Project Report revealed [43] the use of the following chemicals: disulphide compounds (e.g diphenyl disulphide & diallyl disulphide), aliphatic amines (e.g hexadecyclomine for EPDM rubber) and various rubber accelerators (e.g. ZDEC & MBT). The most important mechano-chemical de-vulcanisation technologies are overviewed below:

Levgum technology

This commercially available technology[44] has been developed by an Israeli company, Levgum. The de-vulcanisation is carried out at room temperature using a two-roll mill. The material and chemicals (urea compound and difunctional acid compound to create organic cation) are milled (20 passes) to achieve de-vulcanisation.

De-Link technology

This commercially available technology[45] (e.g. Petra Technologies Inc.) is based on the *De-Link Process*, originally developed and patented by Tan Sri Dr B. C. Sekhar and Vitaly Abramovich Kormer in 1996[46] . The De-Link process is based on the Sekhar-Kormer-Sotnikova reaction[47] (Fig. 7) that opens up the vulcanised rubber network to produce a resultant de-vulcanised compound called "De-Vulc", which (on its own or blended with virgin rubber) can be re-manufactured into a wide variety of products such as belts, hoses, mats, flooring and tyres, without a further addition of vulcanising agent[48]. This technology is efficient for sulphur cured natural and synthetic (e.g. EPDM, NBR, SBR, IIR) rubbers and their blends. Studies showed that the technology works best with conventional sulphur cure systems[4,47]. Moreover, both, filled and unfilled rubber compounds can be de-vulcanised by this process.

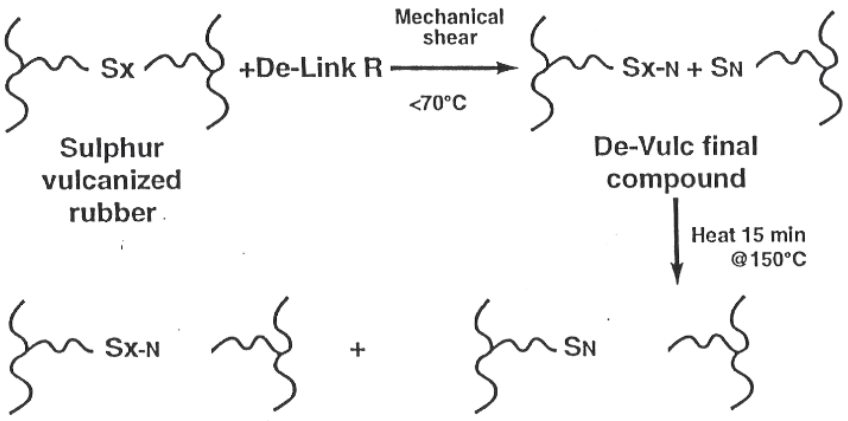


Fig. 7 De-Link Process & Sekhar-Kormer-Sotnikova reaction mechanism[47]

The patented[46] chemical reactant "*De-Link R*" comes in a masterbatch form (a mixture of chemicals in an appropriate rubber binder) and typically consists of zinc dimethyldithiocarbamate (ZDMC) and 2-mercaptobenzothiazole (MBT) accelerators in the molar ratio of 1:1 to 1:12 dispersed in diols (e.g. diethylene glycol) and a small proportion of stearic acid, zinc oxide and sulphur. The de-vulcanisation process is normally carried out on a two-roll mill, below 70ºC and takes around 10 minutes. The recommended ratio of the De-Link R to ELT crumb is 6 parts to 100 parts by weight. However, determining an optimum level of the de-vulcanisation reactant is vital for successful de-vulcanisation and it varies from one formulation to another.

De-Link process overview:

- De-Link R is a mixture of chemicals already used in the rubber industry
- Optimum levels of De-Link R depend on a number of factors, including the vulcanising system of the original (waste) compound and the polymer content in the compound formulation [49]
- The combination of highly active vulcanisation accelerators (e.g. ZDMC & MBT) initiates the proton exchange reaction through the assistance of delinking activators (stearic acid, zinc oxide & methacrylic acid) [46]
- De-link R reactant provided thiophilic nuclephiles (e.g. ZDMC) to break the sulphur crosslinks) and electrophiles (e.g MBT) to trap the crosslink fragments [43]
- Re-vulcanisation is likely to occur prematurely alongside de-vulcanisation if the processing conditions change (e.g high temperature) [43]
- Shear action leads to creation of new crumb surfaces [47]
- For every sulphur crosslink that is de-linked after further vulcanisation two crosslinks are formed [47]
- The new crosslinks are shorter than in the original network [47]
- De-vulcanised material (De-Vulc) is not fully de-vulcanised [49,50]

- The re-vulcanised compound has a complex structure: crosslinks remaining from the original vulcanisation process (acting as a filler) and new crosslinks, forming the new rubber network [51]

Changes in the network structure in the original (waste) and re-vulcanised compounds lead to inevitable changes in physical and mechanical properties. It has been claimed that 50% to 75% of the original material's properties can be retained with this process, potentially allowing a higher content of recycled material to be used as a virgin rubber substitute in more demanding applications, including tyres. The latter is limited by reduced scorch time and deterioration in strength properties, particularly tear strength [48]. In addition, if the de-vulcanisation is carried out as a batch process, the quality of material may vary from batch to batch.

The main changes in the properties of de-vulcanised and re-vulcanised compounds are summarised below:

- Viscosity increases
- Scorch time decreases
- Cure time decreases or increases
- Tensile properties decrease (e.g. elongation at break, tensile strength, tear strength)
- Hardness increases, decreases or remains unchanged
- Resilience increases
- Heat build- up improves
- Compression set improves
- Rolling resistance lowered

An improved patented process [52] offers better handling of the delinking composition as it now comes in a "combined solid form" : pellets or tablets, eliminating the need for glycol to improve the dispersion of the active ingredients in the De-Link R and the need for master-batching. It is also effective with a lower level of the delinking agent (1 to 2 parts per 100 parts of rubber crumb) and higher de-vulcanisation temperatures (between 90º and 105ºC), making the process more suitable for a higher production rate (e.g internal mixer).

Overall, the De-Link technology is commercially available and is effective in de-vulcanising ELT crumb that can be used on its own or blended with virgin rubber in more demanding applications. However, the main limitations of the process are:

- The process does not offer full de-vulcanisation
- De-vulcanisation equipment is limited to a two-roll mill and internal mixer, hence is a batch process

DeVulCO"2 technology

This technology has proven to be successful on a laboratory scale[53] and is now being developed on a commercial scale in the UK (ReMould project)[54]. The technology development is led by Smithers Rapra. It has been patented[55] as a continuous de-vulcanisation process based on a combination of supercritical carbon dioxide ($scCO_2$), de-vulcanisation agents and extrusion equipment. Both single and twin extruders were trialled.

The process uses $scCO_2$ to assist the de-vulcanisation process. $ScCO_2$ is a powerful solvent and is similar in properties to hydrocarbon solvents such as toluene. However, it is considered to be more environmentally friendly and sustainable as it is non-flammable, relatively inert, low toxicity and naturally abundant. Its critical point is easily accessible[56] (critical temperature is 31.1ºC and critical pressure is 7.38 MPa) and signifies its transition from gas to supercritical liquid at and above this point. Applications of $scCO_2$ to assist de-vulcanisation process using either sealed vessels (e.g autoclave) or extruders have been reported by a number of researchers[56–62]. When used on its own, the solvent acts as a "process aid" swelling the rubber (non-polar in nature) and assisting the preferential breakdown of S-S bonds, initiated by the shearing forces of de-vulcanisation equipment. However, when used as a "reaction medium" alongside other de-vulcanisation agents (eg. diphenyl disulphide) it can increase their penetration into the rubber matrix (either in autoclaves or extruders) and hence, potentially improve their effectiveness. Extruders are generally more efficient and commercially attractive as they can deliver a continuous de-vulcanisation process. Another advantage of using $scCO_2$ is that it evaporates from rubber at the end of the de-vulcanisation process and can act as a cooling agent to reduce the temperature of the extrudate and hence, minimise the chance of degradation[40].

DeVulCO"2 process overview:

- A single or twin-screw extruder is used as a reaction vessel to facilitate mixing, shear and heat
- Waste rubber is used in a crumb form (e.g 40 mesh size)
- The de-vulcanisation system employed in this process is a chemical treatment[55] already used in the rubber industry
- Similar to the De-Link technology, the combination of highly active vulcanisation accelerators (e.g. ZDEC & MBTS) is likely to initiate the proton exchange reaction through the assistance of the de-vulcanisation coagents (e.g. stearic acid, zinc oxide and zinc stearate)
- The main de-vulcanisation additives yield thiophilic nuclephiles (e.g. ZDEC) to break the sulphur crosslinks) and electrophiles (e.g MBTS) to trap the crosslink fragments[43]
- Optional additives, such as peptisers (e.g aromatic thiols) may also be used

- Application of $scCO_2$ improves contact between the de-vulcanisation system and the rubber matrix , increases the shear force yielding new crumb surfaces and provides a cooling effect on the extrudate at the end of the de-vulcanisation process
- De-vulcanised material can be directly re-vulcanised without any additional additives (e.g. sulphur)

DeVulCO"2 process is an innovative process that has been specially developed to de-vulcanise tyre waste for manufacturing high-quality products (e.g damping pads, seals etc). It has been reported[53] that even products manufactured from 100% of the de-vulcanised rubber still have a tensile strength of 18 MPa and elongation at break of 350%. Overall, DeVulCO"2 technology has strong advantages over other competitive technologies:

- it is a continuous process but can provide material on a batch scale
- effective de-vulcanisation system (chemicals[55] + supercritical carbon dioxide)
- does not require expensive equipment
- easy to scale up
- de-vulcanisation can be "tailored" to specific end-use requirements

This thesis has focused on the analysis and characterisation of materials, generated during commercial trials (ReMould project) using DeVulCO"2 technology, in order to develop effective and reliable characterisation techniques for de-vulcanised and re-vulcanised rubber and hence provide the manufacturer with a means of monitoring the efficiency of the de-vulcanisation process and to enable quality control.

2.5.4 Microwave de-vulcanisation

This method is based on the use of microwave energy of controlled dose and a specified frequency and energy level to break C-C bonds. Microwave frequency between 915 and 2450 MHz corresponding to microwave energy between 41 and 177 WH per pound is sufficient to sever all cross-links but insufficient to severe polymer chain backbone bonds. Hence, preventing polymer degradation [17].

However, the rubber material used in the microwave process must be polar in order to accept energy at a rate sufficient to generate the heat necessary for de-vulcanisation [11]. In addition, this method is a batch process and requires expensive equipment.

Recently, work has been carried out on microwave de-vulcanisation of various nonpolar rubbers, including BIIR, SBR, and ELT [33,63]. However, this research is still at too early a stage to be considered as a potentially effective de-vulcanisation method for ELT.

2.5.5 Ultrasonic de-vulcanisation

This process was first developed and patented by Petrofsky in 1973 as an application for waste

tyres [64]. Further work on ultrasonic de-vulcanisation was carried out by Okuda and Hatano who patented a batch process in which a vulcanised rubber was de-vulcanised at 50 KHz ultrasonic waves after treatment for 20 minutes under static conditions [65].

A continuous ultrasonic de-vulcanisation method was developed by Isayev in the 1990s [66]. Since then, the method has been further developed by Isayev and co-workers [11,32,33,67] and trialled on different types of rubber, including tyres. This method uses ultrasonic waves to selectively break the chemical bonds in vulcanised rubber. However, structural studies [11] revealed that the process is also accompanied by the breakup of chemical bonds in the main polymer chain (C-C bonds). In addition, ultrasonic de-vulcanisation causes some deactivation of carbon black filler and hence, blending with virgin rubber is required to maintain the properties of re-vulcanised rubber compounds. The process also alters the re-vulcanisation kinetics of sulphur cured rubbers, leading to the absence or shortening of the induction period and hence, associated processing safety issues.

However, the main disadvantage of this technique is the specialist equipment (e.g extruder fitted with ultrasound device) requirement. In addition, the process conditions have to be carefully selected to prevent significant material degradation during the de-vulcanisation stage.

Despite the recent advances [33], the process has only been trialled on a laboratory scale. It requires the design and manufacture of an industrial size ultrasonic extrusion machine to take it to the next level.

2.5.6 Microbial de-vulcanisation

Although vulcanised rubbers are resistant to normal microbial attack, the microbial surface de-sulphurisation of waste tyre has been reported [32,68,69]. This is done by using very fine rubber crumb (100 to 200 mesh) as a feedstock for sulphur consuming microorganisms: *Thiobacillus, Sulfolobus and Rhodococcus*. These bacteria can attack sulphur bonds in vulcanised rubber on the surface only. Therefore, this process is of more use for surface modification rather than de-vulcanisation.

Microbial de-vulcanisation is carried out by mixing ground rubber with media containing appropriate bacterium in a temperature-controlled bioreactor. The slurry is then maintained at a specified temperature and pressure and is rinsed and filtered at the end of the process to remove the microorganisms. Treated rubber also requires drying. In addition, the treatment is very slow and needs further research to improve its efficiency [33].

2.6 Summary

To sum up, reclaiming is the oldest recycling technique in relation to ELT. However, it is highly laborious and involves reclaiming agents associated with a negative public perception and environmental concerns. In addition, the amount of recovered material that can be used in new tyres is limited to 5%.

Emerging de-vulcanisation techniques offer higher quality materials that can be used as a substitute for virgin material in high performance applications to around 20% but not all of them can

be scaled up for commercial use. Limited data is available in the literature in relation to the properties of rubber compounds based on de-vulcanised tyre rubber. In addition, there is a lack of detailed accounts of test conditions, and processing parameters required for comparative analysis.

The review of de-vulcanisation techniques has identified *mechano-chemical De-VulCO"2 technology* as the most promising and environmentally sound material recovery method. It has been proven on a laboratory scale and is ready for commercialisation with great potential for developing high end applications, including new tyres. The attraction of this technique is that it can be adapted (eg. equipment configuration, processing conditions, chemicals) to address variations in recycled rubber composition, hence it can offer a "tailored" de-vulcanisation process. The next stages of process development, compound development and product development require simple, effective and reliable characterisation techniques that are suitable for testing de-vulcanised and re-vulcanised rubber. Existing and emerging rubber characterisation techniques and their relevance to tyre de-vulcanisation has been overviewed and discussed in Chapter 3 of this thesis.

Chapter 3: Overview of techniques to characterise rubber network

This chapter provides an overview and discussion of the well established and emerging characterisation techniques that can be employed for characterisation and evaluation of de-vulcanised and re-vulcanised rubber waste and therefore, provides a necessary background for understanding the extent and originality of the practical work carried out during this research work.

3.1 Introduction to vulcanisation and network structure

In its raw state rubber consists of long randomly linked hydrocarbon chains which can slide past each other. Raw rubber is therefore plastic, weak and a permanently deformable material. The process called vulcanisation, chemically links the rubber chains together by "cross-links" and forms a three-dimensional network, thereby transforming the elastomeric liquid into an elastic solid[11,70]. The rubber network involves chemical and physical linkages which frequently occur together. The chemical cross-linkages are predominantly covalent and thermostable. Physically formed network structures arise from chain entanglements, rings fitted into each other or chain loops as well as from crystalline adhesion points. Possible network structures[71] are given in Figure 3.1.

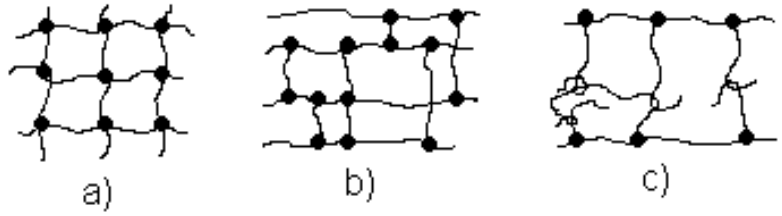


Fig. 3.1 Types of network structures[71]: a) ideal regular network with covalent bonding; b) statistical network with covalent bonding; c) network with chain entanglement

Apart from the type of bond, network polymers differ according to the following:

- constitution of the bridge cross-links
- crystallinity of the segments
- average cross-linking density
- segment length distribution between the points of cross-linking
- number of coexisting phases and their supermolecular structure

The large number of factors influencing network structure gives rise to a very broad spectrum of network properties that require characterisation. The cross-link density parameter has a great influence on physical and mechanical behaviour of vulcanised rubber and is widely used to characterise rubber network[72]. Figure 3.2 schematically shows the main physical and mechanical

properties of vulcanised rubber as a function of cross-link density.

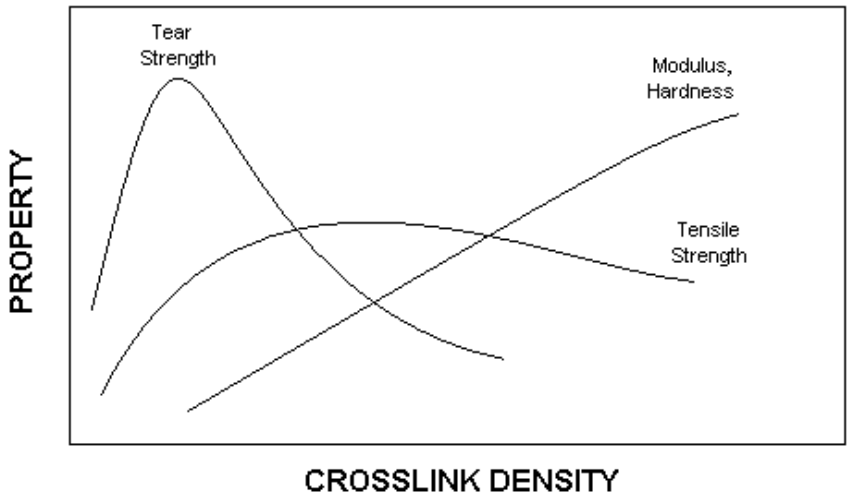


Fig. 3.2 Effect of cross-link densities on mechanical properties of rubber[72]

It can be seen from Fig.3.2 that modulus, hardness and other associated properties (resilience, abrasion resistance and fatigue cracking) increase with cross-link density and the rubber network becomes more elastic and less hysteretic. Fracture properties, such as tensile strength and tear strength, pass through a maximum as cross-linking increases[72]. This behaviour can be explained by the difference in the mechanism of fracture between uncross-linked and cross-linked rubbers. When uncross-linked rubber material is stressed, polymer chains can readily slide past one another and disentangle. At low rates, fracture occurs by viscous flow without breaking chemical bonds. The effect of a limited number of cross-links is to increase the molecular weight by creating branched molecules and therefore, resulting in a broader molecular weight distribution. As it becomes more difficult for the branched molecules to disentangle, the strength properties increase. Further increase in cross-linking leads to gelation and formation of a three dimensional rubber network. Some chains may not be attached to the network (sol component) but the whole composition will no longer dissolve in a solvent. A gel cannot be fractured without breaking chemical bonds. That is why the strength is higher at the gel point, since chemical bonds must be ruptured to create a fracture surface.

However, there comes a point when the strength does not continue to increase further with more cross-linking. This can be explained by the following factor. When vulcanised rubber is deformed by an external force, part of the energy is stored elastically in the chains and is available as a driving force for fracture. The rest of the energy is dissipated through molecular motions into heat and does not lead to chain breaking. At high cross-link levels, chain motions are restricted and therefore the network is incapable of dissipating as much energy. This results in a brittle fracture at low elongation.

Therefore, rubber materials have an optimum cross-link density range for practical use. The cross-linking level must be high enough to prevent failure by viscous flow but low enough to avoid brittle

fracture.

Another important factor influencing the physical and mechanical properties is the type of cross-links. As this research is concerned with sulphur vulcanised rubbers, only sulphur vulcanisation systems will be considered.

The initial vulcanisation process, developed independently by Goodyear in the United States (1839) and Hancock in the UK (1843) was based on heating a blend of natural rubber and sulphur. Since then, special additives have been developed to control the rate and extent of vulcanisation and to improve the properties of vulcanisates. The main types of additives being used with the sulphur or sulphur donor compound in the *accelerated sulphur vulcanisation* are accelerators, activators, retarders and pre-vulcanisation inhibitors.

As the name suggests, the use of accelerators significantly increases the rate of cure, reducing vulcanisation time in some cases from several hours to a few minutes[73]. Accelerators are organic materials that can be divided into the following main groups: guanidines, dithiocarbamates, thiazoles and sulphenamides. Examples of selected commercial accelerators are given in Fig. 3.3 & Fig.3.4.

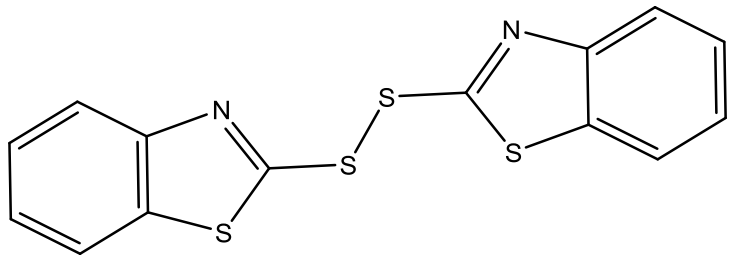


Fig. 3.3 Chemical structure of dibenzothiazol-2-yl disulphide or MBTS (benzothiazole type accelerator)

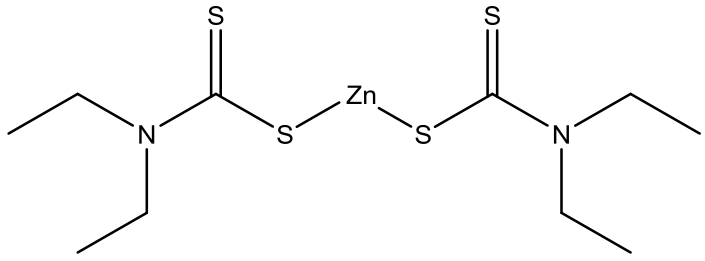


Fig. 3.4 Chemical structure of zinc diethyldithiocarbamate or ZDEC (dithiocarbamate type accelerator)

These types of accelerators are particularly important as they have also been used as the de-vulcanisation reagents in the De-Link and DeVulCO"2 technologies[46,52,55].

Further improvements in accelerated sulphur vulcanisation were achieved through the combined use of the activators: zinc oxide and stearic acid (or another fatty acid) and various organic accelerator systems to give even faster cure times. Although a fast vulcanisation time of rubber products is a desirable feature, it is also necessary to ensure that the vulcanisation reaction does not start prematurely. The total vulcanisation time is comprised of scorch delay time and cross-linking time. Therefore, accelerators are carefully selected for each application to allow a sufficient processing window or time to scorch, which is indicative of the point in time after which a compound becomes elastic and impossible to process[74]. Table 3.1 below shows the comparative vulcanisation rates of the main types of rubber accelerators:

Table 3.1 Vulcanisation rates of main types of rubber accelerators[75]

Accelerator type	**Vulcanisation rate**	**Examples**
Guanidines	medium	DPG, DOTG
Thiazoles	Semi-fast	MBT, MBTS
Dithiocarbamates	Very fast	ZDMC, ZDEC, ZDBC
Sulphenamides	Fast-delayed action	CBS, MBS, TBBS

The scorch delay time and vulcanisation rate of a rubber material is greatly dependent on the nature of the accelerator. For example, sulphenamide accelerators offer an attractive combination of fast vulcanisation rate and delayed scorch time. Depending on vulcanisation rate, a secondary accelerator (e.g. dithiocarbamates type) may be used alongside the main (primary) accelerator to increase the speed of vulcanisation. To delay the onset of the vulcanisation process, special additives may be required. Retarders are commonly used to increase the scorch delay time but they also tend to increase the overall vulcanisation time. Examples of chemicals acting as "retarders" in rubber compounds are phthalic anhydride (PA) and benzoic acid. Pre-vulcanisation inhibitors (e.g. cyclohexylthiophthalimide) are another type of additive used to control the vulcanisation process. In a similar way to retarders they delay the onset of vulcanisation by increasing the scorch time but without having an undesirable effect on the vulcanisation rate.

The overall course of accelerated sulphur vulcanisation of natural rubber is outlined in Fig. 3.5. However, accelerated sulphur vulcanisation is a complex process and the mechanism of individual reactions and their sequence still remain unclear or are in dispute[76].

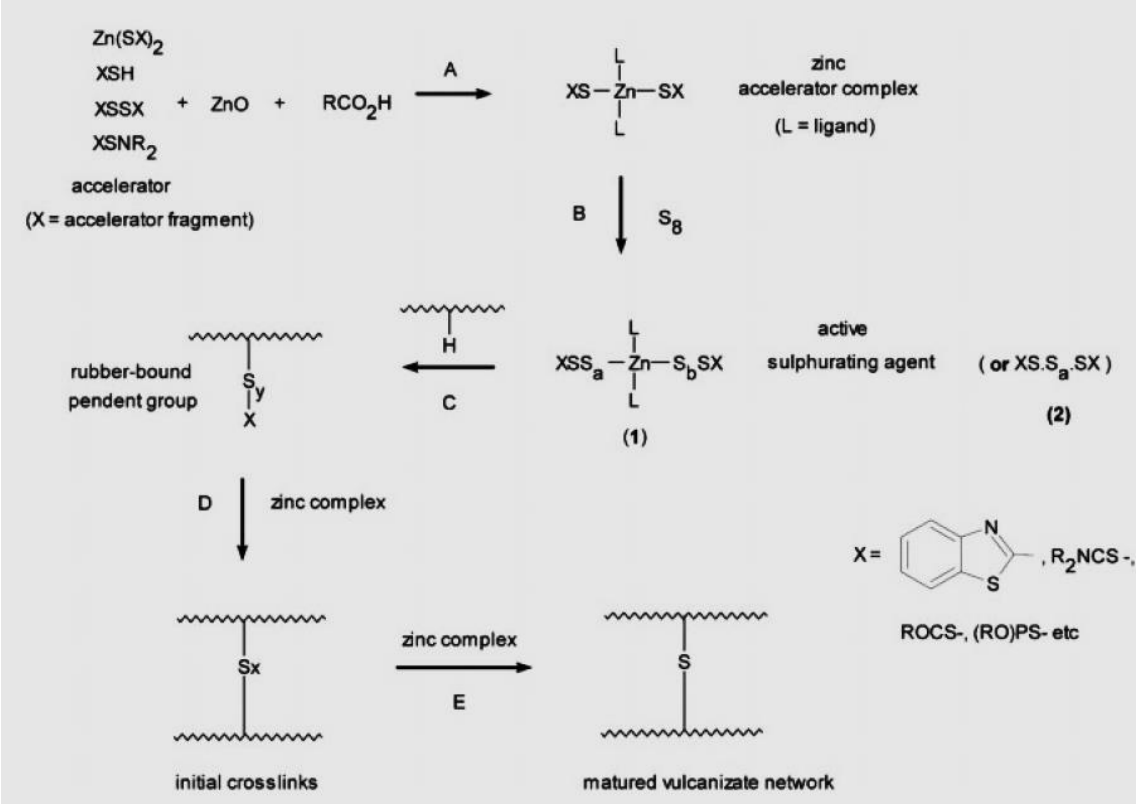
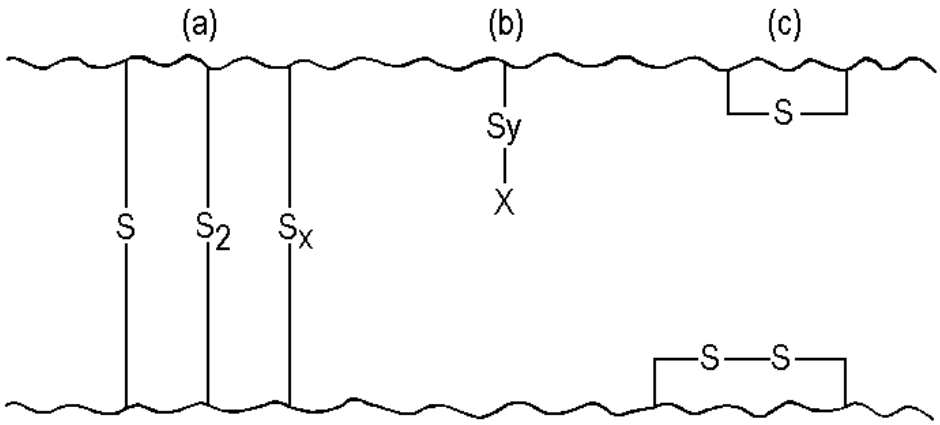


Fig. 3.5 Overall course of accelerated sulphur vulcanisation of NR[77]

The different ways of incorporating sulphur into vulcanised rubber network are illustrated in Fig. 3.6:



a) monosulphide, disulphide or polysulphide
b) pendent sulphides
c) cyclic monosulphides and disulphides

Fig. 3.6 Sulphur cross-linked rubber network[78]

The types of cross-links formed during a sulphur vulcanisation depend on the vulcanisation system employed:

- Conventional
- EV (efficient)
- Semi-EV (semi-efficient)

The difference in the above vulcanisation systems is determined by the level of sulphur and the ratio of accelerator to sulphur in the vulcanisation recipe. Conventional systems are characterised by a high level of sulphur and low level of the accelerator to sulphur ratio as opposed to efficient systems that contain low level of sulphur and a high level of the accelerator to sulphur ratio.

Use of a conventional vulcanisation system leads to a high value of di- & polysulphidic cross-links (95%) and low value of monosulphidic cross-links (5%). On the other hand, employing an "efficient system" (EV) results in a high level of monosulphidic cross-links (80%) and low level of di- & polysulphidic cross-links (20%)[79]. Tyres are usually vulcanised using Semi-EV system to get the right balance in properties. The impact of the vulcanisation system on the final network structure of vulcanisate is illustrated in Fig. 3.7.

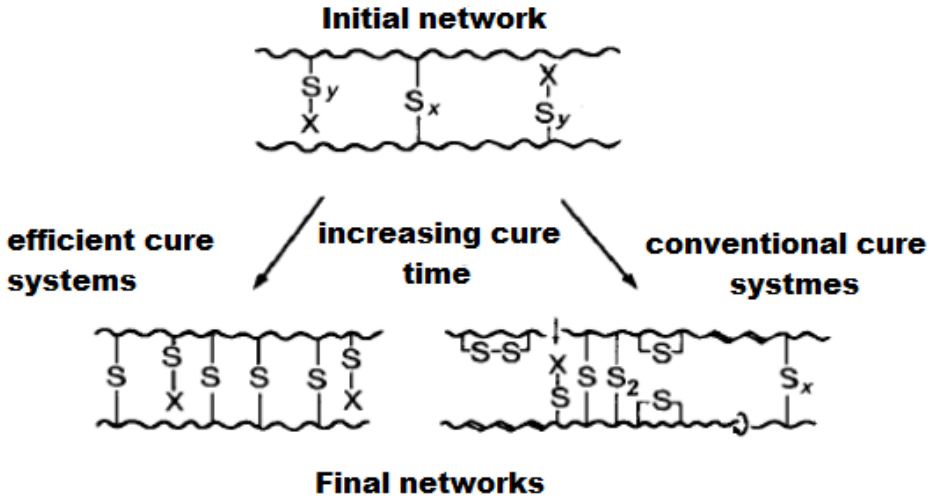


Fig. 3.7 Impact of vulcanisation system on the final network structure[77]

The influence of the type of cross-links on physical and mechanical properties of vulcanisate is illustrated in Fig. 3.8.

As monosulphide cross-links are more thermally stable than di-and polysulphide cross-links, they lead to better heat and thermal ageing resistance properties. However, di- and polysulphide cross-links lead to improved strength properties due to the cross-link scission reactions[76]. Nevertheless, rich in polysulphides cross-links isoprene-based rubber networks are prone to reversion.

Reversion can be defined as the loss of cross-link density as a result of non-oxidative thermal ageing caused by decomposition reactions. Decomposition reactions lead to the loss of cross-links and pendent groups in the network structure and hence, to a deterioration in the properties of vulcanised rubber products at elevated temperatures. The chemical changes in the vulcanisate structure on reversion (e.g. formation of cyclic sulphides, conjugated diene and triene groups etc) also result in rubber products that are more susceptible to oxidation.

As already mentioned, rubber networks rich in mono- and disulphide cross-links are generally less susceptible to reversion. In addition, rubbers with low unsaturation (e.g. EPDM or butyl rubber) are more resistant to reversion due to the lack of neighbouring double bonds to form cyclic sulphides and conjugated trienes.

An increase in vulcanisation temperature increases the rate of decomposition (comparing to cross-linking) and susceptibility to reversion[76]. For example, a relatively stable EV-based rubber network becomes more prone to reversion at temperatures above 140ºC. Published studies also confirmed decomposition of the most stable, monosulphidic cross-links at temperatures approaching 200ºC[80].

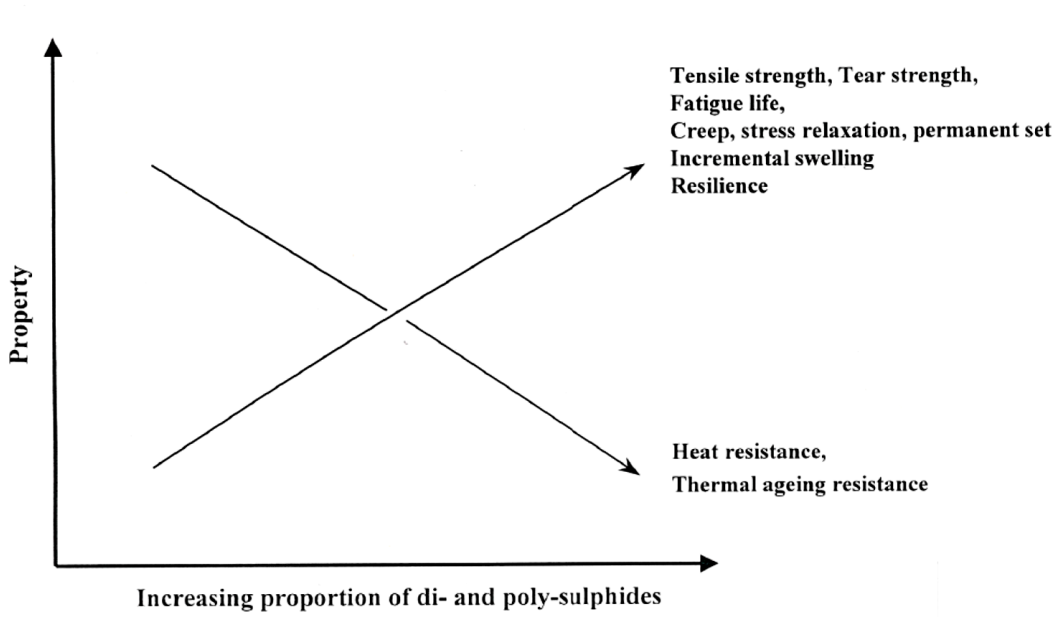


Fig 3.8 Effect of di- and polysulphides on properties[77]

Recent developments in de-vulcanisation technologies (discussed in Chapter 2 of this thesis) highlight the need for practical and reliable technique(s) to characterise and evaluate de-vulcanised and re-vulcanised rubber material produced by de-vulcanisation technologies. This is particularly important at the Research and Development (R&D) stages in working out the optimum de-vulcanisation composition and processing conditions to produce a consistent output. In addition, analysis and evaluation (quality control and quality assurance) are required beyond the development stages to ensure consistency and reproducibility of recycled material over time. The characterisation techniques reviewed in this chapter were selected in view of their usefulness to the

R&D stages (process & product development) of the de-vulcanisation process.

3.2 Mooney viscosity and Mooney relaxation

The viscosity of an unvulcanised rubber compound is an important characteristic of its processability[75]. In general terms, viscosity can be defined as the resistance of a fluid to flow under stress. In relation to raw rubber, a number of methods are available to measure its viscosity, including rotational viscometers or Mooney viscometers.

Viscosity measurement using Mooney viscometers is well-established and is the most commonly used procedure in the rubber industry as it enables the monitoring of the quality and processability of raw rubber and unvulcanised compounds. This technique measures the torque necessary to rotate a metal disc in a cylindrical chamber filled with raw rubber or unvulcanised rubber compound. The measurement is carried out at a low shear rate ($1s^{-1}$) under specified conditions (temperature and time). The result is expressed in Mooney Units (MU), with the Mooney viscosity value being proportional to the value of the torque. The full procedure is detailed in standard[81] BS ISO 289-1:2005. Mooney viscosity characterises the viscoelastic behaviour of raw rubber and relates to its average molecular weight, molecular weight distribution, molecular structure, branching and non-rubber constituents[82].

In addition to measuring Mooney viscosity, Mooney viscometers can provide information on Mooney torque relaxation. Mooney relaxation measurement can give a valuable insight into both, the elastic and viscous components of rubber material. Studies carried out by Enabe et al showed that that high elasticity leads to slow relaxation and vice versa [83]. In addition, the rate of stress relaxation is reported by Malac to correlate with molecular weight distribution, chain branching and gel[82]. Example of a typical curve showing Mooney viscosity and Mooney relaxation in NR at 100ºC is represented in Fig. 3.9.

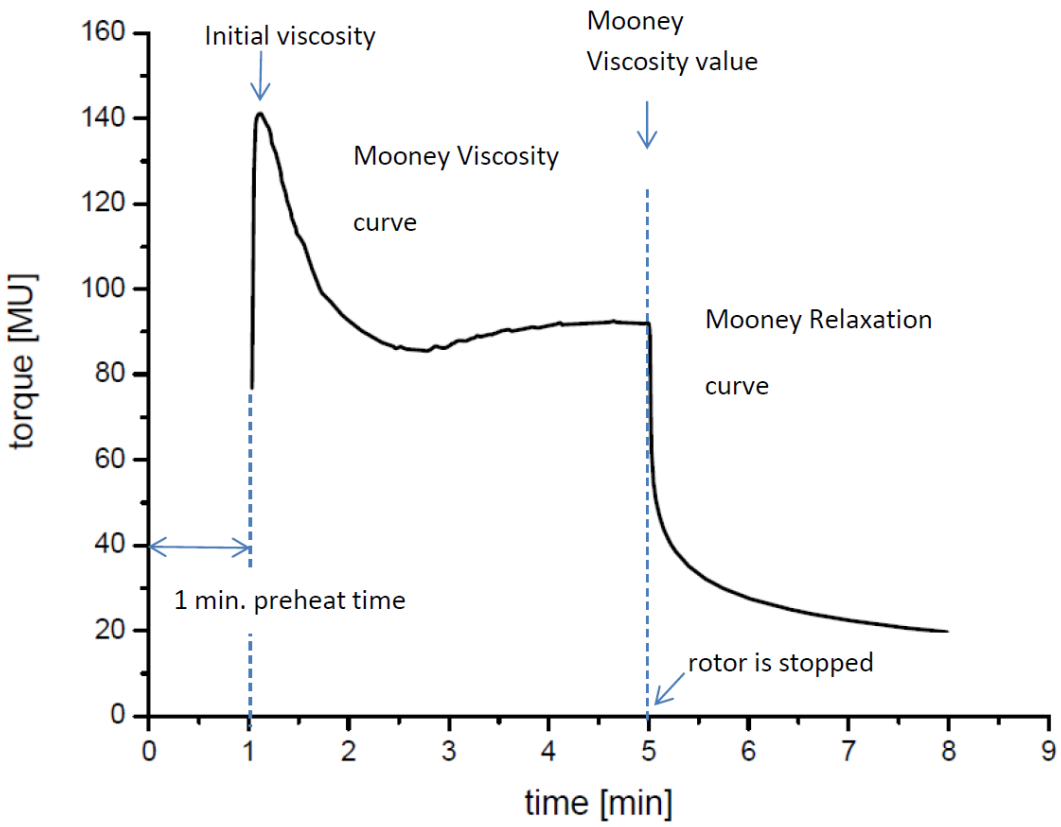


Fig. 3.9 Mooney Viscosity and Mooney Relaxation curve of Natural Rubber[82]

A Mooney relaxation test is carried out on the same sample as is used for viscosity measurements. At the end of the viscosity measurements, the rotor is suddenly stopped and the response of the sample is continuously monitored by recording its torque over a specified period of time.

Mooney relaxation in synthetic and natural polymers can be determined using a power law model:

$$\boldsymbol{M = kt^{a}} \qquad \textbf{(1)}$$

Where:

M is the Mooney relaxation torque

k is the constant equal to torque 1s after the rotor has stopped

a is an exponent that measures the rate of stress relaxation

t is time in s

Equation (1) can be converted into a log-log expression and used for analysis of relaxation data:

$$\boldsymbol{\log(M) = a\log(t) + \log(k)} \qquad \textbf{(2)}$$

The slope *a* can be used as an indicator of uncured rubber elasticity: steep slope meaning low elasticity[84]. As values of the *slope a* are negative, Malac[82] proposed to use *(a+1)* for simple

interpretation of results: higher value of exponent *(a+1)* means higher deformation energy retention in material in time and hence higher elasticity of a sample.

As elasticity is related to cross-link density, Mooney viscosity and Mooney relaxation data can be employed as an indicative measure of the efficiency of de-vulcanisation process, providing information on cross-link reduction and breakage of the main polymer chain.

A number of studies[43,85,86] used Mooney viscosity value as an indicative measure of the extent of de-vulcanisation process. As the Mooney viscosity relates to the modulus, the removal of cross-links during de-vulcanisation leads to reduction in modulus and viscosity value. However, the value of viscosity can also be influenced by changes in both the material's composition (eg. additives) and the processing conditions. In addition, the use of waste rubber crumb from different sources can also present a similar problem.

Work by the Tun Abdul Razak Research Centre[43] was based on de-vulcanisation of waste truck rubber crumb using De-Link R technology and a range of similar de-vulcanisation reagents. This study used Mooney viscosity as an indicative measure of the extent of de-vulcanisation, with the lower viscosities attributed to the greater extent of de-vulcanisation. A small Mooney rotor was employed for pure de-vulcanisates due to their high viscosities. Processing of de-vulcanised material was reported to improve by blending with virgin rubber (25/75 blend: de-vulcanised material/virgin material). Mooney viscosity results reduced with an increased level of de-vulcanisation chemicals or by increasing the length of de-vulcanisation process, indicating improvement in de-vulcanisation efficiency.

Jalilvand et al[85] investigated the de-vulcanisation process of EPDM automotive weather strip material in co-rotating twin-screw extruder with Diphenyl Disulphide as de-vulcanisation agent.
Mooney viscosities were related to different processing conditions (barrel temperature, screw speed and amount of de-vulcanisation agent) and swelling measurements (sol fraction). The results showed that increases in barrel temperature decreased viscosity and increased sol fraction, indicating an improvement in de-vulcanisation efficiency. Mooney viscosity was also related to the molecular weight of the sol fraction and affected by changes in compound formulations (amount of filler and oil). It was observed that tensile strength of re-vulcanised rubber increased with the rise of de-vulcanisation temperature, while the elongation at break increased with the increase in barrel temperature, screw speed and level of de-vulcanisation agent.

Meysami[87] studied carbon dioxide assisted mechanical de-vulcanisation process of waste tyre rubber and EPDM automotive weather strip crumb in a co-rotating twin-screw extruder. The influence of the processing conditions (screw speed and feed rate) on Mooney viscosity, swelling measurements, sol-gel analysis, curing characteristics and physical & mechanical properties were investigated. Tyre compounds showed good correlation between Mooney viscosity and cross-link density & sol fraction values: increase in viscosity was observed with increase in cross-link density

and decrease in sol fraction. Screw speed and feed rate affected viscosity and the de-vulcanisation process: lower viscosity was attributed to higher screw speed and lower feed rates. Mooney viscosity of EPDM compounds was affected by screw speed and feed rate in the same way as the tyre compounds. A correlation was observed between the viscosity and cross-link density values. Sol fractions were affected by the screw speed but not the feed rate on its own. Another study[88] on EPDM waste rubber, de-vulcanised in a Brabender batch mixer using a hexadecylamine as de-vulcanisation agent, reported application of Mooney viscosity as an early indication of the degree of de-vulcanisation: as the de-vulcanisation reaction leads to decrease in cross-link density, resulting in a lower value of Mooney viscosity.

This research will extend the use of Mooney viscosity measurements to include Mooney relaxation data (not currently applied in de-vulcanisation studies) as it can provide valuable information on elasticity leading to more accurate evaluation of the de-vulcanisation process. In addition, the data will be compared to other identified parameters related to the de-vulcanisation process (e.g volume fraction of swollen rubber, sol fraction, and tensile properties). It is expected that this unsophisticated technique can then be used as a quick characterisation tool during the R&D stages, particularly when complemented by a calibration plot of modulus against cross-link density of samples vulcanised to different degree.

3.3 Swelling measurements

Equilibrium swelling is a simple technique that has been widely used to characterise the network structure of unfilled pure rubber vulcanisates[89]. As the vulcanisation process continues, the amount of cross-links increases, leading to increased modulus, hardness and reduced ultimate elongation and permanent set and hence, has to be controlled for optimum performance[90]. Swelling measurements involve physical determination of the degree of cross-linking and are based on the theory of dispersion forces. The swelling capacity of vulcanised rubber in solvent is related to the number of effective cross-links in the same way as the elastic modulus. Therefore, the physically effective cross-link density of rubber can be determined by this technique. In addition, the measurements of equilibrium swelling have been employed to study characteristics of re-vulcanised “double” networks[91] and de-vulcanised and re-vulcanised rubber compounds[92–97]

The covalent rubber network consists of long and flexible chains allowing large and reversible deformations and hence, the ability of cross-linked rubber to absorb the solvent and swell rather than dissolve, as illustrated in Fig. 3.10. Swelling will continue until the retractive forces in the extended chains balance the forces tending to swell the network, reaching the point known as the equilibrium swelling. This technique usually involves extraction of non-rubber components (e.g. accelerators, activators) from a rubber sample with a suitable solvent followed by swelling the sample in a solvent with a similar solubility parameter to the sample to the point of equilibrium. The volume fraction of rubber in swollen vulcanisate, V_r can be calculated from swollen and dried weights of the samples and related to the cross-link density parameter by the Flory-Rehner

equation[70,98] to characterise the rubber network. In addition, the amount of sol (rubber unconnected to the network or soluble part) and gel (rubber network or non-soluble part) can be also quantified.

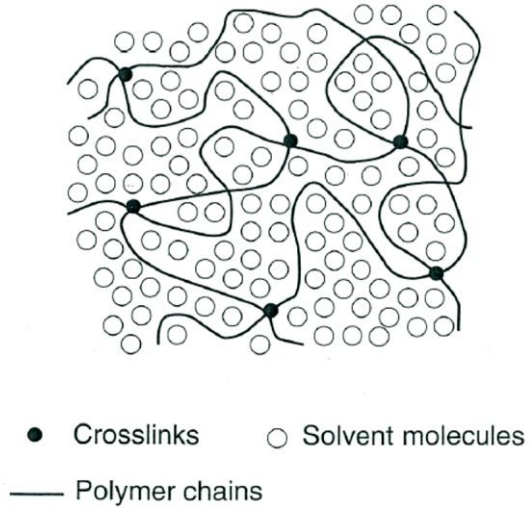


Fig. 3.10 Schematic representation of covalent rubber network swollen by a low molecular weight solvent[99]

The amount of sol, determined by a solvent extraction technique, was reported[40] to measure the effectiveness of the de-vulcanisation process with the amount of extract expressed as a percentage of the weight of the original sample. A greater value of the sol fraction was attributed to a high effectiveness of the de-vulcanisation process to remove cross-links. However, the results can be affected by degradation of rubber during processing and therefore should be analysed alongside additional techniques (e.g. Gel Permeation Chromatography to determine the molecular weight of the sol fraction). The amount of sol in a waste EPDM compound de-vulcanised by a twin-screw extruder, determined by equilibrium swelling, was reported[85] to correlate with the increase in the barrel temperature, indicating the efficiency of the de-vulcanisation process and assisting in selection of the optimum de-vulcanisation conditions. Therefore, solvent extraction on its own or as part of the equilibrium swelling measurement can provide useful information on the effectiveness of de-vulcanisation process.

Analyses of the gel fraction (rubber network) is more complex as the network structure, as explained earlier, is defined by a number of parameters, including the number of cross-links, their functionality and distribution, network defects (e.g. loops) and entanglements. The swelling measurements can be used to determine the average molecular mass between the cross-links, $\bar{M}_c$, related to the expression for the physically effective cross-link density, η_{phys}:

$\boldsymbol{\eta_{phys}} = \frac{1}{2\bar{M}_c}$, the number of moles of cross-links per unit mass (e.g. moles kg^{-1}) **(3)** or

using the rubber density, ρ:

$\boldsymbol{\eta_{phys}} = \frac{\rho}{2\bar{M}_c}$, the number of moles of cross-links per unit volume (e.g. moles m^{-3}) **(4)**

The dependence of $\bar{M}_c$ (equations 5 & 6) on the equilibrium volume fraction of rubber in a swollen ideal network may be described by the Flory-Rehner equation[98], which combines an expression for the free energy change due to elastic expansion of the network during swelling with the Flory-Huggins equation for mixing of liquid with linear rubber molecules of infinite molecular weight:

$$-[\ln(1 - V_r) + V_r + \chi V_r^2] = 2\rho V_s \eta_{phys} V_r^{\frac{1}{3}} \quad \textbf{(5)}$$

Where:

V_r is the volume fraction of polymer in the swollen gel at swelling equilibrium

V_s is the molar volume of the solvent ($cm^3\ mol^{-1}$)

χ is the polymer-solvent interaction parameter

η_{phys} is the physically effective cross-link density

ρ is the density of rubber

Apart from the original Flory-Rehner equation, a modified form of the equation[100] is also used [101] (e.g. to measure the cross-link density in unfilled vulcanised natural and synthetic rubbers to study vulcanisation process):

$$-[\ln(1 - V_r) + V_r + \chi V_r^2] = 2\rho V_s \eta_{phys} (V_r^{\frac{1}{3}} - 0.5 V_r) \quad \textbf{(6)}$$

Both, the original and modified Flory-Rehner equations are only valid for unfilled rubber compounds and hence, are not suitable for tyres or any other rubber formulations where carbon black reinforcing filler (e.g N220 grade in tyres) is used. This is because the presence of the reinforcing filler tends to increase the value of cross-link densities during swelling due to restriction of swelling caused by the filler[102]. In order to compensate for this restriction Kraus[103] and Lorenz & Parks[102] proposed different corrections. Their work was examined and further improved by Porter[104] who developed an empirical relationship between an equilibrium value of V_r in unfilled and filled vulcanisates. However, this correlation is not applicable to tyre waste materials as it requires information on the type and amount of filler.

Additional complications in characterising ELT using the cross-link density parameter from the equation 5 or 6 arises from the fact that the tyre compound is a blend of rubbers (Chapter 2, Table 1: Composition of recycled truck tyre crumb), with each rubber phase having different cross-link density and different polymer-solvent interaction parameter[105].

However, a relationship between the physically effective cross-link density, η_{phys} and the volume fraction of swollen rubber, V_r (equations 5 & 6) allows the use of the former to characterise the rubber network.

In simple terms, the volume fraction of swollen rubber at equilibrium can be defined by the following equation:

$$\boldsymbol{V_r = \frac{volume\ of\ rubber\ hydrocarbon}{(volume\ of\ rubber\ hydrocarbon)+(volume\ of\ swelling\ liquid)}} \quad \textbf{(7)}$$

However, different interpretation of the parameters in equation (7) combined with poorly documented swelling procedure can still lead to significant errors and discrepancies in results. Different approaches to calculate the volume fraction of swollen rubber were reviewed by Valentin et al[106] and the most common sources of errors were outlined. Their review emphasized the importance of the weight correction factor for the insoluble ingredients in a formulation, outlining two extreme models currently employed:

- When all the sample volume is considered as rubber volume
- When all ingredients in the rubber compound, with exception of rubber, are considered insoluble

Their review outlined the most useful and general methods to calculate the concentration of a polymer via gravimetric measurements and recommendations for further corrections in the solvent weight (excess solvent at the insoluble particle/rubber interface) and rubber density (use of compound density).

Based on the review by Valentin and co-workers[106] and published studies[92–97] where the volume fraction of swelling rubber was used to characterise the network structure of recycled rubbers, the following equation has been identified as the most relevant and commonly applied:

$$\boldsymbol{V_r = \frac{\frac{m_d - f m_i}{\rho_r}}{\frac{m_d - f m_i}{\rho_r} + \frac{m_s - m_d}{\rho_s}}} \quad \textbf{(8)}$$

Where:

m_d is the deswollen dry weight of sample

m_i is the initial weight of sample

$m_s$is the weight of sample at equilibrium swelling

ρ_r is the density of polymer

ρ_s is the density of solvent

f is the correction factor (mass of non-rubber ingredients in formulation/mass of all ingredients)

In order to eliminate the errors in calculating V_r, a further correction[107] should be made for the extraction of acetone extractable materials (e.g oils, oligomers, vulcanising agents):

$$V_r = \frac{\left[m_d - m_e(1-E)^{-1}(f-E)\right]\rho_r^{-1}}{\left[m_d - m_e(1-E)^{-1}(f-E)\right]\rho_r^{-1} + \left[m_s - m_d\right]\rho_s^{-1}} \quad \textbf{(9)}$$

Where:

m_e is the dry weight of sample after acetone extraction

E is the weight fraction of acetone extractable material in the sample and is equal to:

$$E = \frac{m_i - m_e}{m_i} \quad \textbf{(10)}$$

In the case of tyre waste material, the amount of polymer and insoluble ingredients (eg. ZnO, fillers) will be accurately determined by thermogravimetric analysis (TGA) and used to account for the insoluble ingredients. In addition, the density of rubber compound will be determined for each material and used in relevant calculations.

To sum up, equilibrium swelling measurement is a widely employed, simple technique that has been successfully used to characterise the rubber network in unfilled pure rubber vulcanisates. However, when applied to blends and/or filled compounds this technique can lead to significant errors, particularly in determination of cross-link density parameter. This review revealed different approaches used to calculate the cross-link density parameter and highlighted the lack of information provided (e.g clear assumptions and definitions) to validate and compare results. As the cross-link density parameter determined by the swelling measurement is only valid for unfilled pure rubbers, the volume fraction of swollen rubber has been chosen for characterisation of tyre waste material, applying corrections identified by the literature review to eliminate common errors.

3.4 Chemical probes

A characterisation technique using chemical probes to test sulphur-vulcanised natural rubber was pioneered and developed for practical use in the 1960s at the Malaysian Rubber Producers' Association (MRPRA). Saville and Watson defined a chemical probe as an analytical reagent which can be homogeneously introduced into the rubber network to react with a specific network feature and can be easily extracted without side reactions once the chemical reaction has been completed. Their review[108] covered triphenylphosphine, thiol-amine reagent, sodium di-n-butyl phosphide, lithium aluminium hydride, phenyl lithium and methyl iodide and provided the means for themselves and subsequent researchers to distinguish between different types of cross-links in carbon black filled NR vulcanisate:

- Monosulphide bonds

- Disulphide bonds
- Polysulphide bonds

Chemical probe techniques have become a valuable accompaniment to swelling measurements by offering information on the types of cross-links. Different ways of incorporating sulphur into the vulcanised rubber network are illustrated in Fig. 3.6 and the influence of the type of cross-link on the main physical and mechanical properties is evident from Fig. 3.8 of this chapter. For example, Russel[109] applied chemical probes to improve the life of truck tyres by relating the content of poly- di- and monosulphide cross-links to defects such as blowouts and tread separation.

The use of chemical probes in relation to network characterisation and partial de-vulcanisation ability is well overviewed and discussed by Warner[110] who identified the following reagents as the most relevant to de-vulcanisation:

- Triphenylphosphine (to cleave polysulphide links) and sodium di-n-butyl phosphite (for di- and polysulphide links)
- Thiol-amine (mainly for di- and polysulphide links)
- Dithiothreitol (for disulphide links)
- Lithium aluminium hydride (for di- and polysulphide links)
- Phenyl lithium (for di- and polysulphide links)
- Methyl iodide (monosulphide links)

However, the drawback of the most effective reagents is that they may pose a health risk as some (e.g. Methyl iodide) have been identified as carcinogens.

Levin et al[111] confirmed that the process of de-vulcanisation by different methods (e.g. heating or thermo-mechanical treatment) is accompanied by the cleavage of polysulphidic cross-links leading to increased amount of the mono- and disulphidic cross-links and reduction in chain mobility. On the otherhand, the cross-link density of de-vulcanised network tends to decrease.

The usefulness of chemical probes in de-vulcanisation of unfilled NR and EPDM and the characterisation of recycled network structure was reported by Verbruggen et al[112]. Their study compared the use of different types of disulphides as recycling agents and employed thiol-amine chemical probes to study the cross-link distribution of recycled materials.

Cross-link densities and cross-link types of original and de-vulcanised samples were determined by swelling measurements combined with thiol-amine reagents. A Horikx plot[113] was used to distinguish between the main chain scission or cross-link scission. The results showed that the use of disulphides in thermo-chemical de-vulcanisation proved to be more effective with NR than EPDM. All poly- and disulphidic cross-links in the original NR vulcanisate were broken at 200^0C. However, main chain scission also took place at this point. EPDM showed low reactivity at 200^0C and improved results when the temperature was raised to 275^0 C.

A typical automotive door seal EPDM compound vulcanised using conventional, semi-efficient and efficient vulcanisation systems was analysed by thiol-amine probes to study the effect of

vulcanisation systems on the cross-link density and type of cross-links by Kuno et al[97]. Their studies revealed that tensile properties, tear strength and the compression set of vulcanised materials were dependent on the overall cross-link density. On the otherhand, the ratios of mono-, di- and polysulphidic cross-links showed a minor effect on these properties. Thiol-amine probes were also reported to study the types of cross-links in NBR compounds[94]. Thiol-amine probes were employed[114] to study the proportion of mono- di- and polysulphidic cross-links of the vulcanised network in diene rubbers (NR and IR).

Overall, the use of chemical probes is a well-studied and well documented technique that has been used to characterise the rubber network by providing information on the types of cross-links in vulcanised rubbers. As the type of cross-links is related to important physical and mechanical properties of rubbers and their product usage, including tyres, application of this technique alongside the swelling measurements can provide additional benefits for the de-vulcanisation process (e.g. optimum processing conditions, type and amount of de-vulcanisation agents) and the quality of recycled material. However, the concentration of different types of cross-links can be only estimated from determination of cross-link densities of the samples before and after de-vulcanisation. For the reasons explained in section 3.3 of this chapter, determination of the cross-link density parameter in *waste* tyre materials can lead to significant errors and therefore have not been chosen for network characterisation studies.

3.5 Thermal analysis

The glass transition temperature, T_g, is an important characteristic of a polymer as it represents the temperature region at which the amorphous phase of polymer transforms from a glassy brittle state into a tough elastic liquid. This characterisation parameter is particularly important to tyre tread compounds as it determines the abrasion resistance, rolling resistance, wet grip behaviour and low temperature performance[115]. Not surprisingly therefore, this parameter has been considered in cross-linking studies[116–118] of elastomers and their blends using Differential Scanning Calorimetry (DSC).

DSC is a thermal analysis technique which is based on measuring the difference in heat flow to a sample relative to a reference material while both are heated or cooled at a constant rate. The changes in heat flow are recorded as a function of temperature and related to the heat capacity. This allows the detection of important transitions in the sample, including T_g.

Cook et al[117] reported the use of a specially developed DSC procedure for cross-linking studies of NR/BR and NR/SBR blends. The instrument operating temperature range was stated to be between -130^0C and -40^0C with a heating rate of 20^0C min^{-1} and a sample weight between 10-14 mg. The instrument was first calibrated by running a raw rubber blend prior to running a vulcanisate. The results were then presented as the shift in T_g arising from vulcanisation. The initial correlation found between physically effective cross-link density and T_g for the individual

polymers was used to estimate the physical cross-link density of their blends and compared with the measurements made by the swollen ^{1}H- NMR technique. The results were better for the NR/BR (70/30) blend than NR/SBR (50/50). However, the general trend showed increased T_g followed an increase in physical cross-link density of blends.

In general, cross-linking decreases the mobility and entropy of the network chains and is expected to increase Tg. Therefore, changes in the glass transition temperature upon de-vulcanisation may be related to changes in the cross-link density, as a reduction in cross-linking is expected in a de-vulcanised rubber network.

However, unexpected results were reported by Levin et al[111] where DSC was used to measure changes in the glass transition temperature of ultrasonically de-vulcanised sulphur- cured SBR compounds. Contrary to the expectation, the results showed a significant increase in the T_g value, from the original to de-vulcanised and further to re-vulcanised compound while the cross-link density of de-vulcanised sample was lower than the original compound as expected. On the otherhand, their comparative work on dicumyl peroxide vulcanised SBR showed no changed in T_g over the same cross-link density range, supporting their conclusion that the predominant influence of changes in the chemical structure (formation of cyclic polysulfidic structures) rather than changes in the cross-link density were responsible for decreased molecular mobility of rubber cross-linked by sulphur.

As emphasized by Chapman and Tinker[118], changes in Tg value cannot be solely amounted for changes in cross-link density as the latter can also be affected by the changes in the vulcanisation system. In addition, they stated that the dependence of T_g on cross-link density is generally low (around $1^{0}C/20mol\ m^{-3}$) for NR and even with very precise DSC measurement provides an uncertain estimate of cross-links. Other known procedures based on DSC analysis and their relevance to the characterisation of the network structure (eg. cure characteristics and freezing point depression) appear to be time consuming, indirect and prone to errors.

In conclusion, DSC analysis using T_g procedure to characterise rubber network may provide an estimate of cross-link densities of pure unfilled elastomers. This technique was also developed to estimate the cross-link density of blends, including NR/BR when coupled with swollen state ^{1}H NMR procedure. However, other factors can also influence T_g leading to misleading estimates of cross-link density. For example, some de-vulcanisation agents and/or de-vulcanisation processes themselves interfere with the network structure and lead to errors in converting changes in T_g to cross-link density. The relevance of this technique has therefore not been investigated any further in the current study.

3.6 Spectroscopic techniques

Infrared Spectroscopy

Infrared Spectroscopy is a characterisation technique that is based on molecular vibration due to the periodic motion of atoms in a molecule while the whole molecule undergoes translational and rotational motions[119]. Examples of vibration modes include symmetrical stretching, asymmetrical stretching, scissoring, rocking, wagging and twisting. Molecular vibrational energy changes as a result of absorption of infrared radiation. All molecules have inherent frequencies of vibration that can be determined by infrared spectroscopy.

In general, infrared spectroscopy can be used to[119]:

- identify a known component present in an unknown sample by comparing the infrared spectrum of the sample with that of known component
- study the formation of new chemical bonds or substitution/modification of existing bonds with new ones
- carry out quantitative analysis for a component of interest
- determine the quality or consistency of a sample

The most useful type of infrared spectrometers is the Fourier Transform Infrared (FTIR) type. This spectrometer produces an interferogram, instead of recording the spectral intensity directly as a function of the wavelength. As the interferogram signal is transmitted through or reflected at the sample surface, the specific frequencies of energy are absorbed by the sample due to the excited vibration of functional groups in the molecules. The recorded interferogram is then converted using Fourier transformation numerical analysis into a plot of intensity and frequency (or wavenumber) called a spectrum. The band intensity (y axis) is usually expressed as a percentage of transmittance or absorbance. The infrared spectrum can be divided into three main regions[120]: the far-infrared (<400 cm^{-1}), the mid-infrared (4000-400 cm^{-1}) and the near-infrared (13000-4000 cm^{-1}). The majority of FTIR instruments operate in the mid-infrared region[121].

FTIR spectrometers can operate in transmission or reflection mode but also in attenuated total reflectance mode (ATR). The transmission mode is the oldest technique and is based on absorption of infrared radiation at specific wavelengths as it passes through a sample. The transmission technique is often used for quantitative analysis of samples in liquid, solid or gaseous forms. However, FTIR instruments working in transmission mode require careful sample preparation, as the quality of the spectrum produced greatly depends on how well the sample has been prepared for analysis. For example, liquid samples have to be filled into special liquid cells and solid samples have to be first diluted with a special infrared inactive salt (e.g. potassium bromide) before being pressed into pellets or thin films for analysis. Therefore, reflectance techniques may be more appropriate for those samples, such as rubbers that are difficult to analyse by conventional transmittance techniques.

Attenuated total reflectance (ATR) technique has been extensively used in the last 20 years as it requires minimum or no sample preparation. ATR-FTIR is based on total internal reflection when infrared reflection is attenuated by absorption within a surface layer a few micrometers deep[122]. During ATR-FTIR measurement, a sample in a solid or liquid form is directly brought into close contact with the ATR crystal, which is made from a material with a very high refractive index (e.g. diamond or germanium). The resultant attenuated radiation is measured and plotted as a function of wavelength by the spectrometer. Other reflectance techniques (e.g. specular reflectance, diffuse reflectance) are mainly used in the study of surfaces. They are based on external reflectance of infrared radiation directly from the surface of the sample.

The use of FTIR in de-vulcanisation studies has been reported by M. Forrest[40] where it was used to investigate the approximate polymer composition of tyre waste compounds (e.g natural rubber, peak at 890 cm^{-1}; styrene-butadiene-styrene rubber, peak at 700 cm^{-1}; butadiene rubber, peak at 966 cm^{-1}). Prior to FTIR characterisation, the samples were first extracted to remove process oil and other low molecular mass organic compounds and then pyrolysed to cancel the effect of the fillers present.

ATR-FTIR was employed in the network characterisation study[94] of electron beam irradiated nitrile rubber, which compared the intensities of the peaks (695 cm^{-1} and 636 cm^{-1}) corresponding to C-S-C stretching vibration due to monosulphidic cross-links. However, the chemical probe treatment of irradiated samples and the solid-state NMR characterisation technique were also employed to validate the results. The samples characterised by the FTIR technique in this study were in the form of thin films.

FTIR was also reported[123] to characterise the soluble part of the de-vulcanised NR samples produced by the solid state mechano-chemical milling process and compare them to the soluble part of the virgin material. Although, the FTIR results of the de-vulcanised samples were very similar to the virgin sample, showing all characteristic peaks of NR and no new peaks in the spectra, the molecular weight of the de-vulcanised samples determined by the GPC technique was reduced ($\bar{M}_w$ by approx. 22%), indicating some degradation of the main chain.

A similar study[124] on de-vulcanised NR samples, based on the mechano-chemical de-vulcanisation process, used the FTIR technique to compare re-vulcanised and virgin samples directly. Spectra were taken from 4500 to 650 cm^{-1} in the transmission mode. The absence of the peak at 1730 cm^{-1} (carbonyl stretching) in re-vulcanised samples spectra was considered as an indication of the absence of oxidative degradation during milling.

FTIR coupled with GPC (Gel Permeation Chromatography) was also reported[95] to characterise soluble parts of unvulcanised, de-vulcanised and re-vulcanised black-filled EPDM samples, produced by a mechano-chemical de-vulcanisation process using a twin-screw extruder. The

samples were first extracted in acetone and then in toluene. The sol fraction in toluene was then dried in a rotavapor prior FTIR analysis. It was noted that the peaks indicating the formation of hydroxyl and carbonyl groups (approx. 3500 cm^{-1} and 1700 cm^{-1} respectively) were not present in the spectra of the samples, indicating the absence of thermal degradation in EPDM. A peak at 1740 cm^{-1} (carbonyl stretching) in virgin samples was explained by the presence of the vulcanising agents (e.g stearic acid, ZDBC and ZDMC). In general, the spectra of all samples appeared to be quite similar while the molecular weight determined by the GPC varied.

To sum up, FTIR has been used in de-vulcanisation studies to compare the chemical composition of de-vulcanised, re-vulcanised and virgin rubbers. The traditionally used transmission technique requires sample preparation and on its own does, not appear to be sensitive enough to guide optimisation of the de-vulcanisation process by detecting relevant structural changes in rubber materials. However, the ATR-FTIR technique requires minimum sample preparation and may provide a useful tool to identify polymer composition and compare the consistency of the recycled material prior to de-vulcanisation, particularly in the case of ELT.

Nuclear Magnetic Resonance spectroscopy

Nuclear Magnetic Resonance (NMR) is a spectroscopic technique that can quantitatively detect the presence of certain chemical elements by measuring the amount of energy absorbed from a radio frequency coil surrounding the sample[125]. This technique is based on the magnetic properties of nuclei of certain atoms that can be detected using a strong external magnetic field. Useful nuclei for NMR spectroscopy in relation to polymers[126] are ^{1}H and ^{13}C. On application of a strong external magnetic field, these nuclei exhibit the low-energy orientation (parallel to the external magnetic field) and the high-energy orientation (antiparallel to the external magnetic field). Transition of a nucleus between these two orientations leads to absorption or emission of energy.

^{1}H-NMR or proton magnetic resonance spectroscopy is based on the magnetic properties of the hydrogen nucleus, one of the most frequently and widely used nucleus due to its high natural abundance (more than 99%) and high sensitivity.

With this technique, a polymer sample is first dissolved in appropriate solvent, yielding a viscous polymer solution, which is then introduced into an NMR sample tube. Application of relatively high temperatures during the NMR process leads to a better spectral resolution. However, the optimum temperature for the test should be selected to sustain the sensitivity. The most commonly used NMR spectrometers are the pulse FT spectrometers that use a very short RF pulse with sufficient power to excite/irradiate all the nuclei of a given species simultaneously. The signal observed in this method is called Free Induction Decay (FID) signal. Fourier Transformation is used to transform FID signal into the normal frequency domain NMR spectrum.

A typical NMR spectrum shows intensity of an NMR signal as a function of frequency. For convenience, absolute frequencies on the horizontal scale of the spectrum are replaced by the

difference between the position of the signal of interest and a reference and referred to as the chemical shift. Furthermore, as the frequency difference in Hz depends on the magnetic field, it is usually expressed in parts per million (ppm) to remove this dependence. Tetramethylsilane (TMS) is used as a reference for ^{1}H-NMR, with the position of the resonance 0.0 ppm (parts per million) on the chemical shift scale and designated shifts to the lower applied magnetic field are considered positive, where as those to the higher application magnetic field are considered negative. The majority of chemical substances, including polymers are found to the left of TMS. As solid samples do not offer high resolved spectra, they have to be dissolved in a solvent that has different background absorption for the same type of nuclei to that in the sample. Deutero-chloroform ($CDCl_3$) is usually used as a solvent as it contains a hydrogen isotope instead of the hydrogen atom. The residual solvent in a sample gives a small peak, easily distinguishable from the peaks in the sample. Every peak in the ^{1}H-MMR spectrum has a characteristic line width, with some peaks showing multiple structures, arising from interactions between protons through chemical bonds.

^{13}C-NMR spectroscopy is based on the magnetic properties of ^{13}C nucleus that has a low natural abundance (1.1%). It is also much less sensitive than the ^{1}H nucleus but yields sharp signals and has a wide chemical shift range. ^{13}C spectra are usually measured under the proton decoupling condition. The same as with ^{1}H-NMR spectroscopy, TMS is used as a reference standard and $CDCL_3$ is often employed as a solvent. ^{13}C-NMR spectroscopy usually requires larger samples and longer acquisition time than ^{1}H-NMR. For example, when studying a unit structure or composition of a copolymer a sample concentration of 50-100 mg cm^{-3} is required to compare to only 5-20 mg cm^{-3} in case of ^{1}H-NMR. Similarly, for the same procedure, acquisition time increases from a few minutes to an hour or longer with ^{13}C-NMR technique, particularly in the case of end-group or branching analysis[127]. Chemical shift in ^{13}C-NMR spectrum arises in the same way as in ^{1}H-NMR: each carbon nucleus has its own electronic environment and absorbs at different field strengths.

Common areas of applications[126] of high resolution solution NMR spectroscopy in relation to polymers are:

- stereochemistry
- copolymers
- polymerisation reactions
- end group analysis
- molecular weight

Polymers can also be analysed in a solid state using high resolution solid- state NMR spectroscopy. It is related to applications concerned with heterogeneity (e.g. amorphous & crystalline phases) of polymers, blends and orientation in solid polymers. High resolution solid-state NMR spectroscopy has been also reported useful[128] in cross-link density studies, as the latter is related to the size of pores or cavities inside solid polymers. However, it involves more

complicated techniques, requires more expensive equipment than solution state NMR and specialised knowledge to interpret results [129]. In addition, high resolution solid-state NMR spectroscopy has been used in cross-linking analysis of single elastomers rather than blends[118].

Swollen state ^{1}H-NMR spectroscopy

Some polymers, including rubbers do not dissolve in solvents to give a viscous solution but rather swell to give gels due to their cross-link structure. Therefore, this restriction in movements in polymer chains of rubbers leads to significant line broadening and can obscure chemical shift information normally available in *^{1}H-NMR*. It was noted that for gel analysis the ^{13}C-NMR technique may provide a better spectrum as the broadening is less significant[127]. In addition, the difficulties of studying ELT using ordinary solution NMR spectroscopy arises from their complex constitution as they are generally a blend of three different rubbers.

Since the early development stages of NMR Spectroscopy, polymers have been extensively studied by this technique as outlined earlier in this chapter and the relationship between molecular mobility and line width of relevant peaks was recognised. Continuing interest in this area led to the development and successful application of the specialised characterisation technique: swollen state *^{1}H-NMR spectroscopy* to estimate the extent of cross-linking in vulcanised rubber blends that was first reported[130] by Loadman and Tinker in 1989. This technique (*CW-^{1}H-NMR*) was originally developed using a continuous wave spectrophotometer but was later (1992) extended to Fourier Transform instruments. As this technique can be potentially applied to characterise the network changes in de-vulcanised and re-vulcanised ELT, it has been reviewed in more detail in the last part of this chapter.

The original study carried out by Loadman and Tinker[130] was based on gum vulcanisates of NR and Acrylonitrile-Butadiene Rubber (NBR). The paper demonstrated that the peak broadening in the continuous wave ^{1}H-NMR spectra of swollen vulcanisates could be related to the cross-link density in gum vulcanisates of NR and NBR. Application of *swollen state ^{1}H-NMR* technique was then extended to study the degree of cross-linking in individual phases of NR/NBR physically mixed vulcanisates and vulcanised blends. Small samples (approx. 1 mm x 1mm x 10 mm) were placed in 5mm NMR sample tube with $CDCl_3$ to reach the equilibrium swelling. A small amount of hexamethyldisiloxane containing a trace of chloroform was added as a marker to provide a locking signal at 1.00 ppm. Spectra of the swollen samples were obtained over the range 11 to 1ppm. The olefinic signal was used in the evaluation of the spectra of both NR and NBR.

One of the most important parameters in this technique, *H%* is the ratio of the signal strength at a reference point on the high field of the peak to the signal strength at the peak as illustrated in Fig. 3.11 and equations 11 &12. The position of the reference point is selected on the basis of providing a good range of *H%* over the range of cross-link densities of interest.

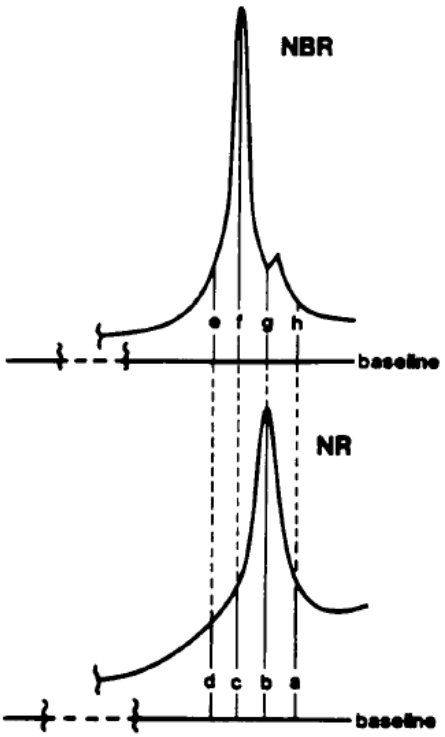


Fig. 3.11 Schematic of NMR spectra[130] of swollen NR and NBR vulcanisates showing the measurements to calculate parameter, *H%*

For NR: $\boldsymbol{H\% = 100\ \frac{a}{b}}$ **(11)**

For NBR: $\boldsymbol{H\% = 100\ \frac{e}{f}}$ **(12)**

This parameter increases as the peak broadens, corresponding to increase in the cross-link density. Therefore, in practical terms, calibration curves can be produced to relate parameter *H* to the physically effective cross-link density, η_{phys} (estimated from other established techniques). In addition, correlations may be also made with V_r that can be considered as a direct measure of cross-link density in an appropriate solvent, or other indicators of cross-link density (e.g rheometer torque rise).

Swollen state ^{1}H-NMR technique is well reviewed and described in the studies[105,131–133] carried out by Tinker and co-workers.

Applications of this technique to study cross-link density of various rubber blends have been extended to include the following elastomers:

- NR/BR(polybutadiene rubber) blends[134–137]
- ENR(epoxidised natural rubber)/BR blends[138]
- NR/Acrylic rubber blends[139,140]
- NR/EPDM blends[141,142] (however, the saturated part of the blend was analysed using ^{13}C NMR)

Apart from being used to study gum rubbers, this technique has been reported[118,131] to be equally

suitable for network characterisation of black filled rubber materials.

Other relevant examples of using NMR spectroscopy to characterise the rubber network

Solid- state ^{13}C NMR spectroscopy & relaxation and ^{1}H- NMR relaxation & pulsed gradient spin-echo self-diffusion measurements at 70^0C have been reported[143] to study molecular and segmental mobility in unfilled NR samples, de-vulcanised by an ultrasonic technique.

Berriot et al[144] applied solid-state ^{1}H- NMR spectroscopy to the characterisation of cross-link density of reinforced elastomers at the filler-elastomer interface. Reinforced elastomers were composed of grafted nanosilica particles and cross-linked ethyl acrylate chains. The NMR measurements were performed on non-extracted samples at 120^0C. The measurements related the transverse relaxation with the cross-linking and/or entanglement densities. Measurements were performed on gum and reinforced samples, comparing the time relaxation of the transverse magnetisation using Hahn echoes. A comprehensive review of solid-state NMR technique in relation to network characterisation of rubbers is written by Ponnamma and co-workers.[145]

Chae et al[146] reported the use of liquid state ^{1}H- NMR to estimate the cross-link density of black filled NR vulcanisates. The ratio of carbon black (N330) was varied from 20 to 80 pphr (parts per hundred rubber) and aged (70^0C for 100 days) and unaged samples were used in the study. Vulcanised rubber strips were first soaked in toluene (1day) and then placed into 5 mm NMR tube with $CDCl_3$ to submerge the strips. In this technique toluene molecules were used as probes to explore the inner cavities of the rubber sample. After the phase correction, the NMR spectra were referenced by setting the internal TMS frequency to 0 ppm. The chemical shifts of ring protons and methyl protons were measured and the data was imported to Microsoft Excel. Changes of chemical shifts were plotted against the carbon black content or cross-link density (determined by swelling measurements). The peak width was measured by fitting the peak to a Lorentzian line shape after the baseline correction. The results showed a correlation between the chemical shift difference (between toluene signal from the bulk solvent and from inside the rubber) and the apparent cross-link density.

In conclusion, solid-state NMR spectroscopy has been used in cross-link studies of ultrasonically de-vulcanised unfilled rubbers, generally NR. However, it involves complex techniques, expensive equipment to compare to solution-state NMR and is more difficult to interpret. As highlighted by this review, the *swollen state ^{1}H-NMR* technique, developed by Tinker and co-workers, appears to be the most suitable technique for the network characterisation of rubbers and their blends, including carbon black filled compounds. In addition, this technique has been successfully applied to a wide range of elastomers. Although, it does not provide a direct measurement of cross-link density, the data obtained can still be correlated to the cross-link density and/or its indicators (e.g. V_r or rheometer torque rise) obtained by other techniques.

Therefore, the *swollen state ^{1}H-NMR* technique has been selected to characterise the de-vulcanised and re-vulcanised rubber materials used in this research work.

3.7 Summary

A review of indicative and more comprehensive techniques to characterise a rubber network has been provided in this chapter. The usefulness of each technique in relation to de-vulcanised and re-vulcanised rubbers and the potential application of each technique to this research has also been considered.

Mooney viscosity measurements have been identified as a useful indicative characterisation technique relevant to recycled rubbers. Apart from the Mooney viscosity, this review also revealed the potential benefit of using Mooney relaxation data (not currently applied in de-vulcanisation studies) to more accurately evaluate the de-vulcanisation process by providing additional information on elasticity.

The volume fraction of swollen rubber (V_r), obtained from the equilibrium swelling measurements, has been identified as the most suitable network characterisation parameter in cases of ELT that are composed of more than one rubber and contain carbon black filler.

ATR-FTIR requires minimum sample preparation and has been chosen as a useful tool to identify polymer composition and compare the consistency of recycled material prior to de-vulcanisation, particularly in the case of ELT.

The *swollen state ^{1}H-NMR* technique, developed by Tinker and co-workers, has been identified as the most suitable and effective spectroscopic technique for the network characterisation of carbon black filled rubber blends and hence, has been selected to characterise the de-vulcanised and re-vulcanised ELT materials used in this research.

Chapter 4: Experimental Work

4.1 Materials

Rubber materials used in this research work were generated during industrial trials that formed the development stages of the new de-vulcanised technology, DeVulCO"2 explained in chapter 2 of this thesis. After being proven successful on a laboratory scale this technology was taken to the commercial level (October 2009) as part of the two year *ReMould* project funded by the Technology Strategy Board (TSB) under their Sustainable Materials and Products Programme.

The aim of the *ReMould* project was to develop an industrial process for the continuous production of re-mouldable and re-vulcanisable rubber compounds for extrusion and moulding purposes (compression, transfer or injection moulding), derived from end-of-life NR, SBR, NBR and EPDM vulcanised rubber, sourced from scrap tyres and other commercial products. The following partners formed a consortium to deliver eight work packages:

- Smithers Rapra
- J. Allcock and Sons Limited
- BD Technical Polymer Limited
- PJH Partnership
- Martins Rubber Company
- Charles Lawrence International
- Kingpin Tyres Limited
- London Metropolitan University

In the capacity of the principal researcher for the *ReMould* project (London Metropolitan University) the task of the author was to characterise, analyse and test the de-vulcanised and re-vulcanised compounds, blends and final products. With the agreement of the TSB and the consortium partners, the materials from these commercial trials were used to form this research study. Due to the nature of the work, details of the de-vulcanisation technology used to produce these materials (e.g. equipment configuration, processing conditions, de-vulcanisation agents etc) cannot be disclosed, apart from information that is already in the public domain (e.g patents). For similar reasons, the specific product formulations of the materials used in this work are also not disclosed.

The materials generated during the *ReMould* project (Fig. 4.1) can be divided into the three main groups: NR-based, NBR- based and EPDM-based (all sulphur vulcanised). In each case, waste rubber crumb (40 mesh size) was de-vulcanised using the DeVulCO"2 technology[55] and the quality of de-vulcanised material was evaluated by comparing it to the virgin material and their blends as detailed in Fig. 4.1.

Accurate evaluation of de-vulcanised material, even for the same type of product (e.g. tyre), proved problematic due to variations in the waste material obtained from different sources. This was

certainly the case with the waste tyre crumb that originated from more than one source. To eliminate the inconsistency of tyre waste crumb a truck tyre tread material of known formulation was subjected to a typical tyre re-treading process at Kingpin Tyre Ltd (Shrewsbury, UK) to produce rubber crumb for the de-vulcanisation purpose as illustrated in Fig. 4.2. De-vulcanised by the DeVulCO"2 process crumb was then blended with virgin material to produce the "closed-loop blends" as detailed in Table 4.1 that formed the central part of investigation for this research work.

All rubber crumb was produced using an ambient grinding technology at J. Allcock and Sons Ltd (Manchester, UK). The de-vulcanisation of rubber waste was carried out by Smithers Rapra (Shrewsbury, UK) and blending was performed by BD Technical Polymer Ltd (Corby, UK).

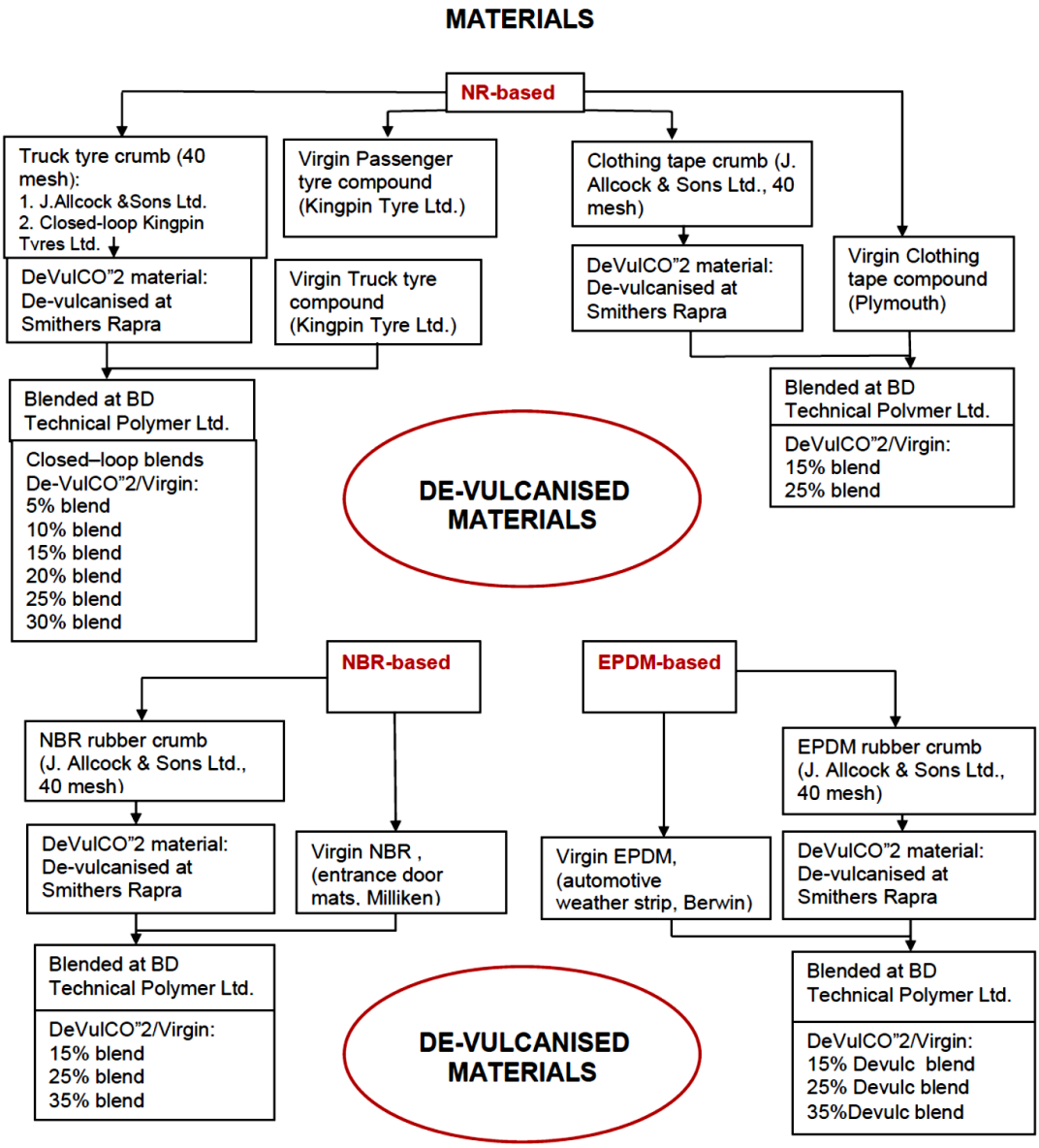


Fig. 4.1 Materials produced during the *ReMould* Project

Table 4.1Closed-loop tyre blends compounds

Sample	Truck Tyre Tread Virgin rubber, %	DeVulCO"2 Truck Tyre Tread crumb, %
Virgin rubber	100%	0%
5% blend	95%	5%
10% blend	90%	10%
15% blend	85%	15%
20% blend	80%	20%
25% blend	75%	25%
30% blend	70%	30%
DeVulCO"2 rubber crumb	0%	100%

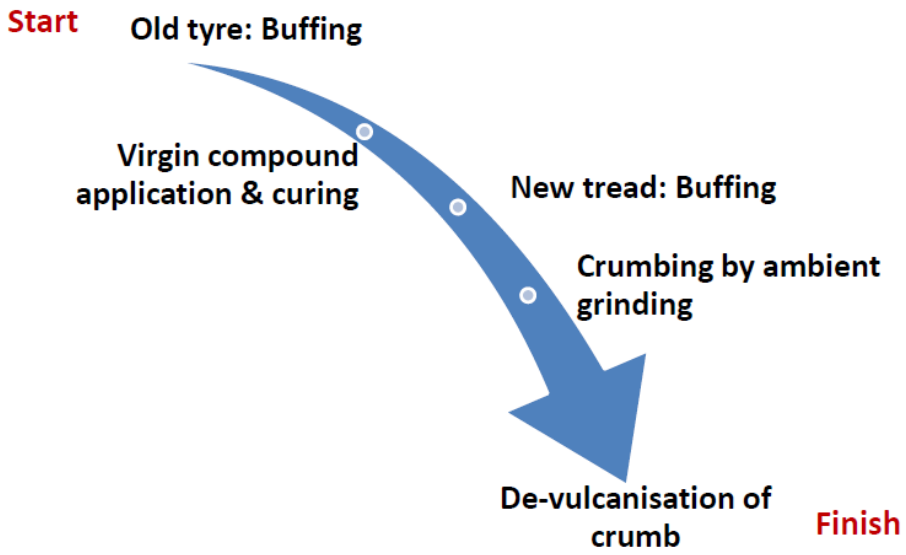


Fig. 4.2 "Closed – loop" process to generate consistent de-vulcanisate

It should be noted that due to the nature of the *ReMould* project (one off commercial trials), it was not possible to reproduce the rubber materials produced during this development stage. In addition, the de-vulcanised materials had a limited shelf life of approximately 6 months thus impacting the design of the experimental work. Hence, material selection for experimental work was driven by availability of materials. For this reason, application of a logical experimental design sequence, using the same material, was not always possible.

All other materials (solvents) used in this work were of a reagent grade by Fisher Scientific Limited

(unless stated otherwise) and were used as received without further purification.

4.2 Mooney viscosity and Mooney relaxation

Mooney viscosity measurement was carried out in accordance with standard[81] BS ISO 289-1:2005.

Equipment:

Mooney Viscometer (A.Macklow-Smith Ltd, model R23/415)

Procedure:

The viscosities of de-vulcanised rubber materials and their blends with a virgin masterbatch were measured on a shearing disk viscometer at 100° C using a small rotor (30.48 mm). The sample preheat time was 1 minute and the running rotor time was 4 minutes.

The test results were expressed in Mooney units (M) followed by S (small rotor) and test conditions: (1+4) 100^0C.

For example: 10MS(1+4)100^0C, where:

10M is the viscosity in Mooney units

S is small rotor

1 is preheat time in minutes

4 is rotor running time in minutes

100^0C is the test temperature

Mooney relaxation was performed on the same equipment and samples, at the end of the Mooney viscosity test. The rotor was stopped suddenly and the torque was monitored after 1 second and every 10 seconds (for up to 200 seconds) to obtain the relaxation data as explained in section 3.2 (chapter 3) of this thesis.

Three samples were tested in each case to calculate the final result. All samples were conditioned at room temperature for 2 hours prior to testing. Each sample consisted of two parts: 30 mm X 30 mm with approximate weight of 13 gram each. A hole was pierced through the centre of one square part of the sample for insertion of rotor stem. The second square part was placed on the top as showed in Fig. 4.3.

Fig. 4.3 Sample assembly in Mooney viscometer

4.3 Processability and Curing characteristics

Processability

Apart from evaluation of the efficiency of the de-vulcanisation process it was important to ensure that uncured de-vulcanised material and/or its blends with a virgin masterbatch could be effectively shaped by traditional rubber processing equipment (e.g. extrusion, calendaring) as a good surface finish in some applications (e.g. automotive weather strip, tyres) is equally as important as the retention of high performance properties.

The extrudability of de-vulcanised rubber compounds and their blends with a virgin masterbatch were evaluated and compared to a virgin masterbatch of the same type using a Plasti-Corder Brabender extruder (Fig. 4.4) equipped with a Garvey type die (Fig. 4.5) in accordance with the standard[147] ASTM: D2230 using rating system B. According to this standard a rubber material is extruded through a specially shaped die that produces an extrudate having a combination of relatively flat surfaces, sharp corners and thin sections. The quality of the extrudate is then rated visually in terms of smoothness of the surface and the sharpness and continuity of the 30^0 edge. In addition, the die swell of the extrudate can be evaluated and related to the extent of de-vulcanisation by comparing the cross-sectional area of extrudate to the Garvey die (0.5 cm^2).

Equipment:

- Plasti-Corder Brabender extruder (Model PLE 651) with Garvey die
- Bridge two-roll mill

Fig 4.4 Plasti-Corder Brabender extruder

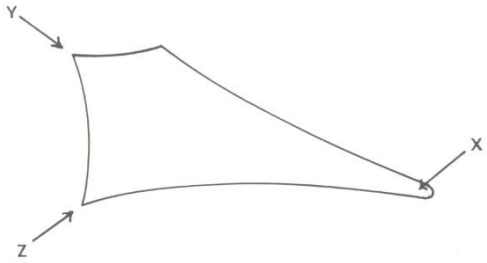


Fig. 4.5 Garvey die where X represents the edge, Y and Z represent the corners

Procedure:

The extruder was pre-set to the following conditions: barrel temperature=70^0 C, head temperature= 110^0 C, die temperature=110^0 C and screw speed=45 rpm.

Prior to extrusion, each sample was first warmed up by banding it on a two-roll mill and cut from side to side at 30 seconds intervals for 4 minutes. The temperature of the stock at the end of the warm-up period was recorded. The sheeted compound (thickness 2±0.2mm) was cut into strips (Fig. 4.6).

Fig. 4.6 Preparation of milled closed-loop samples for extrusion

The strips were then continually fed into the extruder until stable conditions were achieved and a sample of extrudate of approximately 250 mm long could be taken for rating and swelling measurement. The length and weight of each sample was accurately measured and recorded. At the end of the run, the barrel was completely emptied of material by purging before moving on to a new rubber compound.

Curing characteristics

The curing characteristics of the rubber materials were determined by the oscillating disc Monsanto rheometer 100. This instrument was used to produce rheometer charts (torque against time plot) for all unvulcanised compounds. In addition to their traditional use, curing characteristics can be also related to the extent of de-vulcanisation in re-vulcanised compounds by comparing their minimum torque values.

The most relevant data from the rheometry measurements are:

- the torque rise ($M_H - M_L$) which is related to the amount of cross-links introduced;
- the minimum torque (M_L), which is a crude indication of the extent of de-vulcanisation); and
- scorch delay time (ts_2) related to processing safety

Equipment:

Oscillating Disc Monsanto Rheometer 100S

Procedure:

Measurements were carried out in accordance with standard[148] BS ISO 3417: 2008. Conditions under which vulcanisation traces were obtained on the rheometer were: temperature 150±3°C, arc 3°; torque 0-100 dN m; timescale 60 min.

Torque at 90% cross-linking was determined[149] using equation (4.1) and a corresponding time (t_{90}) was used as an optimum vulcanisation time to prepare vulcanised samples for consequent testing. Additional time was added to t_{90} if a sample was thicker than 1 mm: 1minute per additional 1mm increase in thickness. In case of marching curves (continuing increase of torque with time), the maximum torque, M_H was selected as the maximum torque corresponding to 60 minutes.

$$\boldsymbol{M_{90} = \frac{90}{100}(M_H - M_L) + M_L} \qquad \textbf{(4.1)}$$

Where:

M_{90} is the torque at 90% cross-linking, dN m

M_H is the maximum torque, dN m

M_L is the minimum torque, dN m

Cure rate index, *I* was calculated from equation (4.2):

$$I = \frac{100}{t_{90}+t_{s2}} \quad \textbf{(4.2)}$$

Where:

I is the cure rate index, min^{-1}

t_{90} is the time to 90% cross-linking, minutes

t_{s2} is the scorch time, minutes

The maximum rate of cure was estimated from the maximum slope observed in the near linear region of the rheometer cure as illustrated in Chapter 5 (Fig. 5.20).

4.4 Swelling measurements

Sample preparation:

Samples for swelling measurements were vulcanised at 150^0C, according to the estimated optimum vulcanisation time (t_{90}) using a compression moulding press (Daniel Electrical press with square platens 254mm X 254 mm, 4" diameter RAM and 20 t up stroke). A special mould, consisting of 10 cavities with dimensions of 12mm X 12 mm each, was made and used to ensure the samples were the same size. The thickness of the samples was approximately 1mm.

Unvulcanised samples, made of 100% de-vulcanised tyre compound were also used for swelling measurements. The material (crumb or sheet) was first milled on a two-roll laboratory mill to produce a sheet of rubber of approximately 1mm thick. Square samples of approximately 0.05 grams were then produced by punching unvulcanised sheets with a dumbbell die (type 2, BS ISO 37:2005[150]) using a single stroke of a hand press and another stroke was applied to a dumbbell specimen to cut a square sample from its narrow portion.

Equipment: Bridge two-roll mill, Daniel Electrical press, Gallenkamp vacuum oven, Grant Instruments Ltd water bath, Barnstead Electrothermal heaters and Adventurer ™ Ohaus analytical balance.

Procedure:

Extraction

Rubber compounds were first extracted by use of an appropriate solvent[129] to remove the non-rubber substances (activators, accelerators, ets). Acetone was used for all NR-based compounds (including closed-loop tyre compounds).

Acetone extraction technique:

Three samples were weighed using an analytical balance and located in separate thimbles. Each thimble was loaded into the main chamber of a Soxhlet extractor and attached onto a flask containing 120 ml of acetone and a small amount of anti-bumping granules as illustrated in Fig.4.7. The vessels were connected together so that the incoming and outgoing water lines to the reflux condensers could be connected in series. The solvent was heated to allow reflux over the samples for 48 hours.

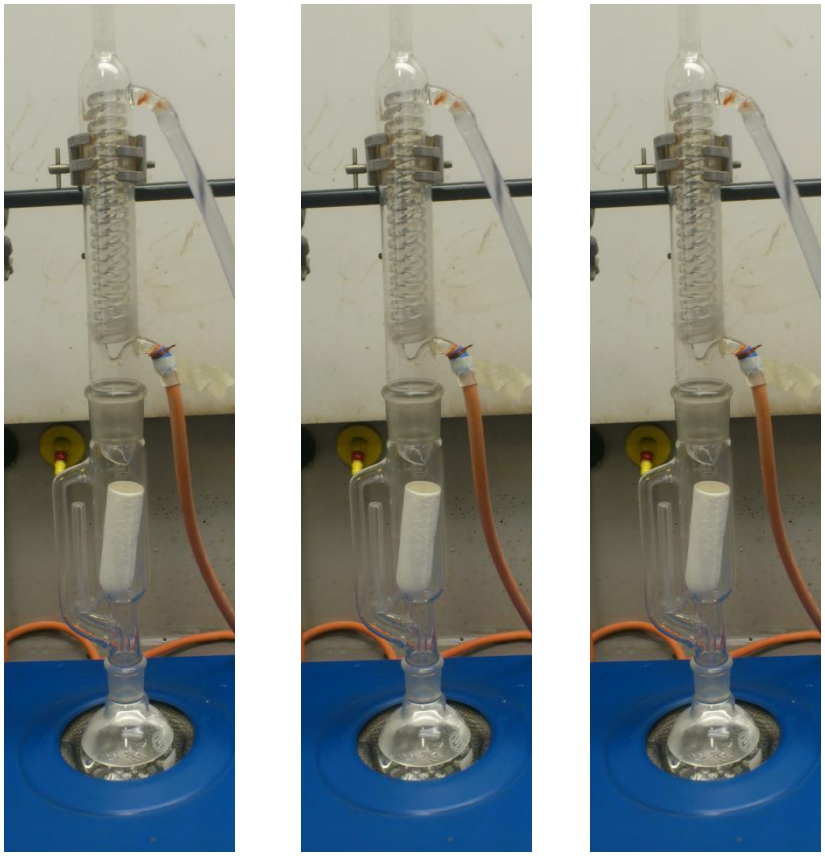


Fig. 4.7 Equipment set up for initial extraction of samples

After 48 hours the samples were taken out of the solvent and dried for 4 to 5 hours in a vacuum oven at the maximum pressure to a constant weight. The temperature of the vacuum oven was set to 50 ± 1^{0}C and a mixture of dry ice and industrial methylated spirit (IMS) was used for the cold trap. The samples were kept in a desiccator for around 30 minutes after drying to cool down before

weighing. The difference in the dried weight of the extracted sample and the original sample yielded the amount of soluble non-rubber components. The samples were stored at room temperature in the desiccator in the dark until required.

Swelling

Three extracted samples of the same compound were weighed (m_e) and placed into separately labelled vials. Ten millilitres of the appropriate solvent was added to each vial. The vials were then sealed and placed into a vial rack and carefully positioned into a temperature controlled water bath so that the level of water in the bath was above the level of solvent in the vials. The swelling was carried out in the dark and water was topped up frequently during the experiment to maintain the correct level. The water temperature of the water bath was maintained at 25 ± 0.5^0C.

The solvent in each vial was refreshed after the first 24 hours and the weight of each sample was monitored daily until it reached diffusion equilibrium (constant weight). To check the weight of the sample the following technique was employed. Each sample was taken out of the vial and the adhered liquid was rapidly removed by blotting it carefully with filter paper before placing the sample into a weighing bottle. The weight of the sample was recorded and the sample was returned to the vial. The vial containing the sample was placed back into the water bath. On reaching the swelling equilibrium, the swollen weight (m_s) of each sample was recorded. Final weightings (m_d) of the samples were then taken after drying them in a vacuum oven at 50 ± 1^0C to a constant weight.

In the case of unvulcanised samples, consisting of 100% de-vulcanised material that disintegrated upon swelling, the combined weight of the vial, sample and solvent was recorded each time till equilibrium swelling was attained. The samples were then placed on pre-weighed filter paper to follow the same drying procedure as with the vulcanised samples.

The swelling results were used in equation 9 (Chapter 3) to calculate the volume fraction of swollen rubber compounds.

Swelling solvents

The solvents used for swelling each type of rubber material were selected in the light of solubility parameters[151]. Cross-linked rubber materials swell in solvents of similar solubility parameter (within $\pm$ 2.0MPa$^{1/2}$ range[152]). As the closed-loop truck tyre samples contained more than one rubber, the solubility of the rubber blend was calculated using the solubility parameter values and the amount of the individual components (Table 4.2). The polymer blend content was based on the composition of a typical recycled truck tyre crumb (Table 2.1, Chapter 2). Based on these calculations, the matching solvents to swell the closed-loop tyre samples were selected from the following range: 16.68 ± 2.0MPa$^{1/2}$ i.e 14.68 – 18.68 MPa$^{1/2}$.

After consideration of the solubility parameters[151] of readily available solvents, the following solvent was selected:

- Toluene (solubility parameter 18.2 $MPa^{1/2}$) was selected for swelling all NR-based compounds (including closed-loop tyre compounds)

Table 4.2 Solubility parameter of a truck tyre tread crumb

Polymer	**% content**	**η / $MPa^{1/2}$ (solubility parameter of individual components)**	**η in blend /$MPa^{1/2}$**
Polyisoprene (NR)	71.0	16.5	11.72
Polybutadiene	11.0	17.1	1.88
Styrene-butadiene rubber	18.0	17.1	3.08
Truck tyre tread	100.0	-	16.68

Density of rubber compounds

The density of rubber compounds was determined in accordance with BS ISO 2781: 2008[153] using method B. Distilled water at a temperature of 25^0 C was used in the test and care was taken to remove air bubbles adhering to the rubber and to the walls of the bottle.

After measurement, the density of rubber (p_r) was determined using the following equation:

$$\boldsymbol{\rho_r = \frac{w_2 - w_1}{w_4 - w_3 + w_2 - w_1}} \qquad \textbf{(4.3)}$$

Where:

w_1 is the weight of the density bottle, grams

w_2 is the weight of the density bottle + test piece

w_3 is the weight of the density bottle +test piece + water

w_4 is the weight of the density bottle filled with water

These measurements were used to calculate the volume fraction of swollen rubber (equation 9, Chapter 3).

4.5 FTIR spectroscopy

Equipment:

FTIR Nicolet 380 Spectrometer with built in Smart Orbit ATR accessories (diamond crystal), coupled with Omnic software.

Samples:

- Waste rubber crumb was analysed as received
- De-vulcanised rubber was supplied in sheets and analysed as received
- Re-vulcanised rubber was first extracted in appropriate solvent and both extract and extracted rubber were analysed

Procedure:

The ATR attachment was used and the spectrum was obtained by pressing the solid sample against the diamond window using the pressure clamp. In the case of the liquid sample (extract and solvent) 4 drops were applied to the top diamond plate using pipette. In this work, the spectrum wavelengths were in the range of 400 - 4000 cm^{-1} and 32 scans were made with a resolution of 28.928 cm^{-1}.

The peak area of the selected peaks was measured using the Omnic software “peak area” tool. First, a spectrum of each sample in absorption mode was subjected to an automatic baseline correction and then the peak area within the selected range of wavelength was determined as illustrated in Fig.4.8 and Fig.4.9. The same region and baseline range was maintained for all samples for the same peak.

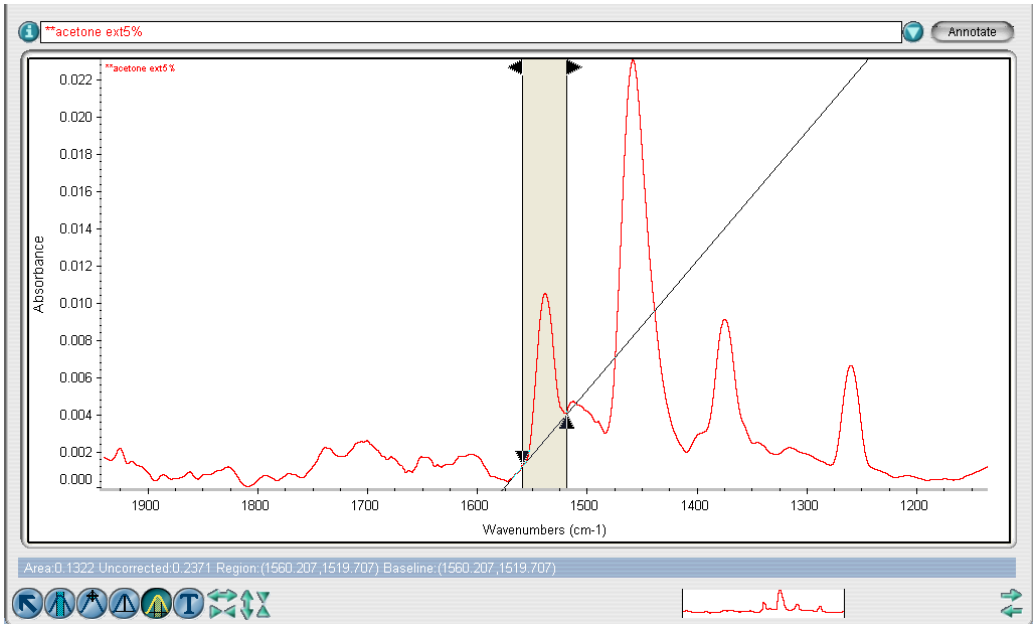


Fig. 4.8 Peak area analysis of the 1540 cm^{-1} peak

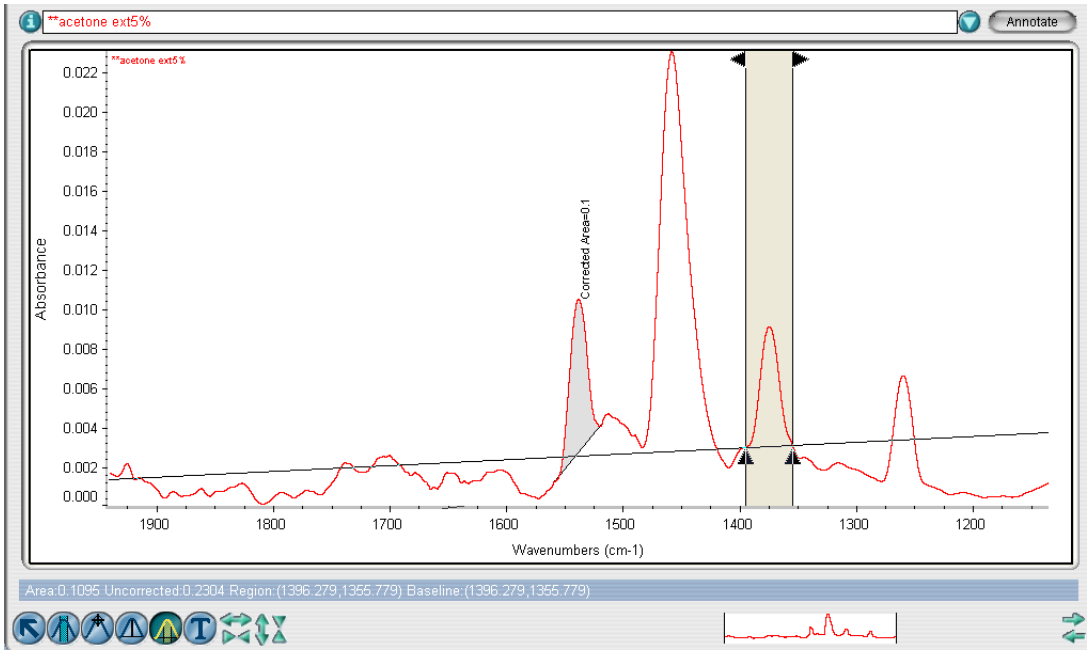


Fig. 4.9 Peak area analysis of the 1375 cm^{-1} peak

4.6 NMR spectroscopy

Swollen-state ^{1}H-NMR spectroscopy technique

In this work, the samples de-vulcanised by DeVulCO"2 technology were analysed in relation to their olefinic signal peak width. Diene-based polymers have their residual olefinic protons in a clear part of the spectrum and are therefore available for NMR analysis. Peak shape and width is a function of the solubility and mobility of the polymer chains. Hence, swollen state ^{1}H- NMR spectroscopy can be used to estimate cross-link density.

Equipment:

Bruker Avance FT Spectrometer 500 (fitted with a gradient shimming probe)

Samples:

Vulcanised samples were used apart from DeVulCO"2 rubber crumb that was used without re-vulcanisation. The samples (selected closed-loop tyre materials) are detailed in Table 4.3

Table 4.3 Materials used for NMR analysis

Sample	Truck Tyre Tread Virgin rubber, %	DeVulCO"2 Truck Tyre Tread crumb, %
Virgin rubber	100%	0%
15% blend	85%	15%
25% blend	75%	25%
30% blend	70%	30%
DeVulCO"2 rubber crumb	0%	100%

Swollen-state ^{1}H-NMR sample preparation technique:

Vulcanised strips of rubber of approximately 2mm x 20mm in size and a small amount of crumb (De-vulc) were first extracted with methanol for 4 hours in a hot Soxhlet apparatus[133] to remove non-rubber components that would otherwise contribute sharp signals with a peak intensity disproportionate to their content in the vulcanisate.

Extracted samples were then pre-swollen in chloroform-d (99.8% deuterated grade, supplied by GOSS Scientific,) to equilibrium swelling in the dark and trimmed while wet to fit and freely rotate inside the NMR tube. The diameter of the NMR tube was 5 mm and the samples (except rubber crumb), were trimmed with a sharp razor blade to approximately 3.5 mm width and 3 mm length.

The prepared samples were placed in the NMR tubes with a fresh solvent and left for at least 1 hour before NMR data was collected. As rubber does not dissolve, but swells in an appropriate solvent, it can be challenging to find a way of keeping a solid sample in the part of the NMR tube from which the data is collected. This proved to be a particular difficulty, in the case of de-vulcanised rubber crumb, where tight packing failed to provide any data and under packing resulted in the crumb rising to the surface (due to the differences in the density of rubber and solvent) and so the data was collected from the extract rather than the rubber itself (Fig. 4.10 and 4.11).

Fig. 4.10 Position of samples in a NMR tube: 30% blend sample (left) and DeVulCO"2 rubber crumb (right)

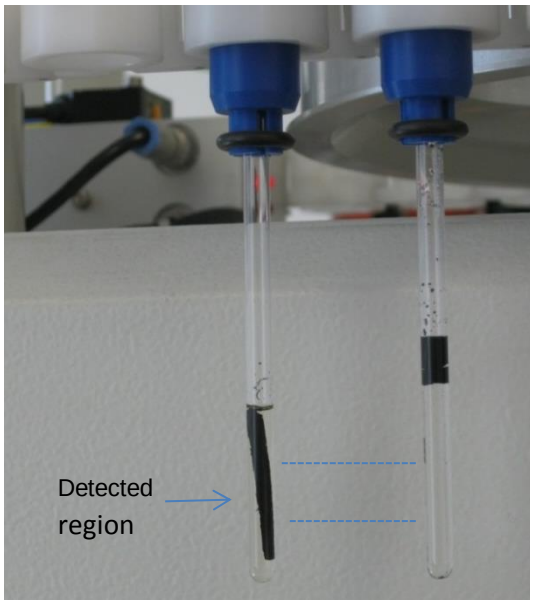


Fig. 4.11 Position of samples in a NMR tube: 30% blend sample (left) and DeVulCO"2 rubber crumb (right)

Swollen state ^{1}H-NMR spectroscopy procedure:

The NMR spectra were obtained using a Bruker Avance FT Spectrometer 500, fitted with a gradient shimming probe. The procedure was based on the methodology developed at TARRC[154].

1. *Standard line shape test:*

To eliminate any possible operational problem related to peak width determination, the standard line shape test was carried out first. To check ^{1}H line shape a sample of 1% chloroform in acetone-

d_6 was used. Tuning the sample solution did not show any irregularities in the line shape and hence, the instrument was ready for use.

2. *Acquisition parameters:*

The following acquisition parameters were used:

Table 4.4 Acquisition Parameters for Swollen State

Parameter	**Value (Units)**
Sweep width	10330.58 (Hz)
Pulse width	3.15 (µsec)
Pulse length	30.00 (degrees)
Delay between pulses	2.00 (sec)
Acquisition time	3.17 (sec)
Number of scans	128

The acquisition of all samples was accompanied by uniform spinning and shimming. Gradient shimming was used to improve the observed NMR line shape for a given sample.

3. *Data processing:*

Test data was initially acquired as free induction decay (FID) and then transformed into the spectrum. No line broadening function was used.

The most important part of the data processing was to obtain symmetrical peaks for the residual H in the solvent at 7.22 ppm and for TSM at 0.00 ppm. In order to achieve this, the peaks were phased manually. Manual phasing ensured a smooth curve of the baseline through the TMS and the chloroform peaks using a consistent approach for all samples. The final spectra of the samples are represented in Fig. 4.12 to Fig.4.17.

To carry out analysis of relevant peaks and calculate parameter H%, the spectrum data (intensity and frequency) of each sample were imported to Microsoft Excel. The olefinic peak of the spectrum was used to calculate parameter H%. In each case, the reference point was located 0.6 ppm downfield from the olefinic peak frequency.

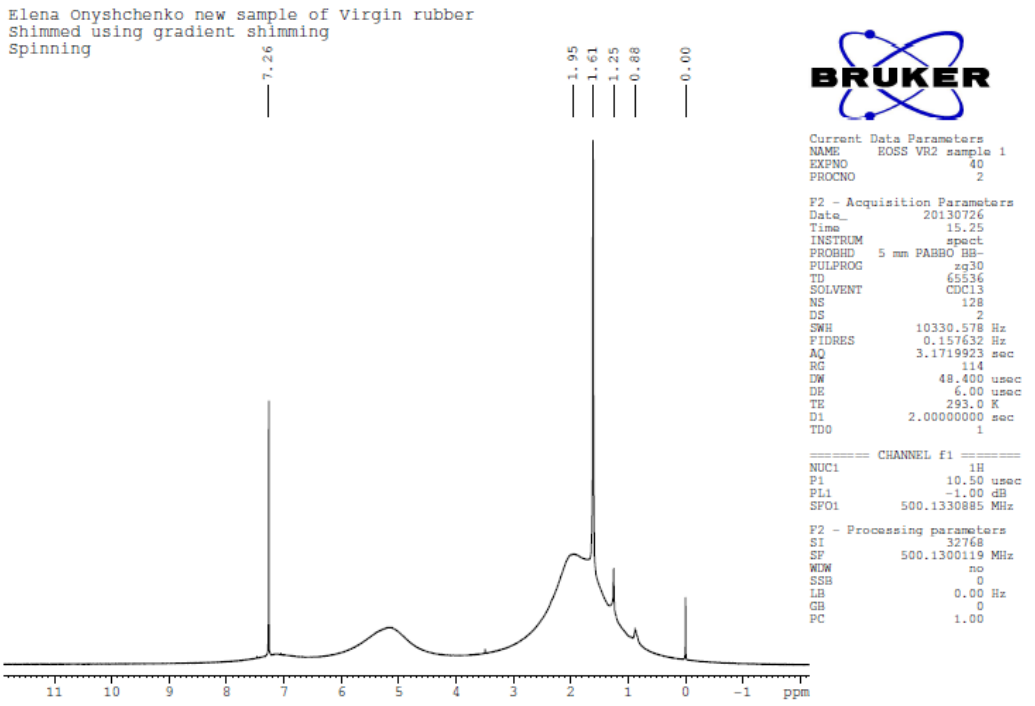


Fig.4.12 NMR spectrum of Virgin rubber sample

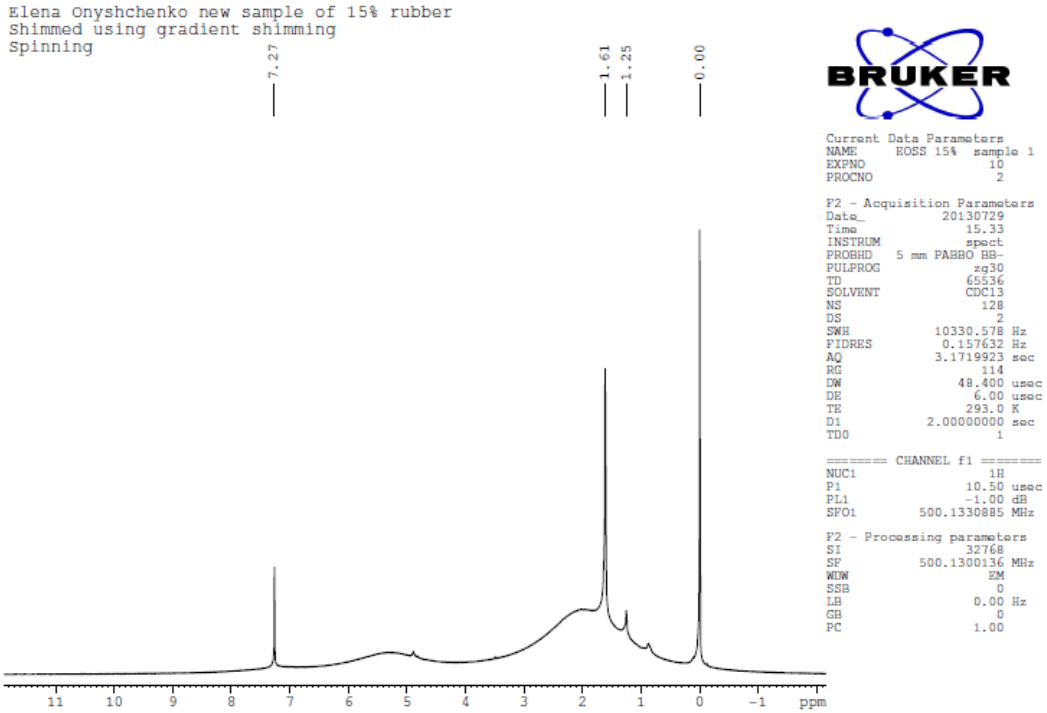


Fig.4.13 NMR spectrum of 15% blend sample

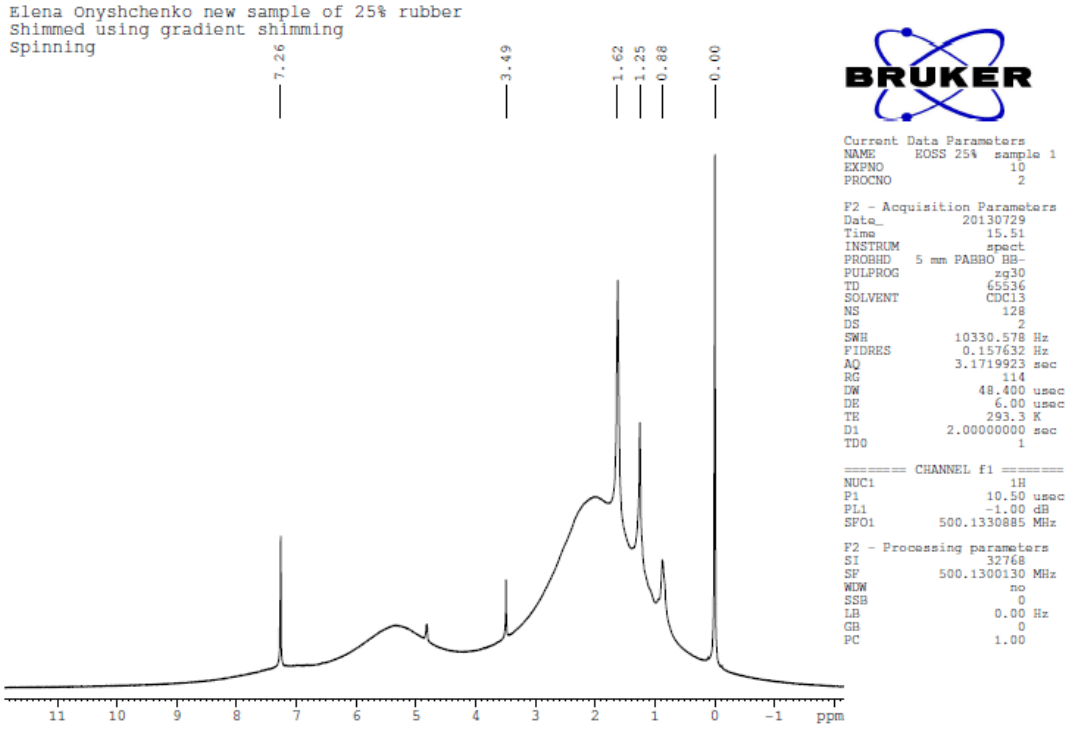


Fig.4.14 NMR spectrum of 25% blend sample

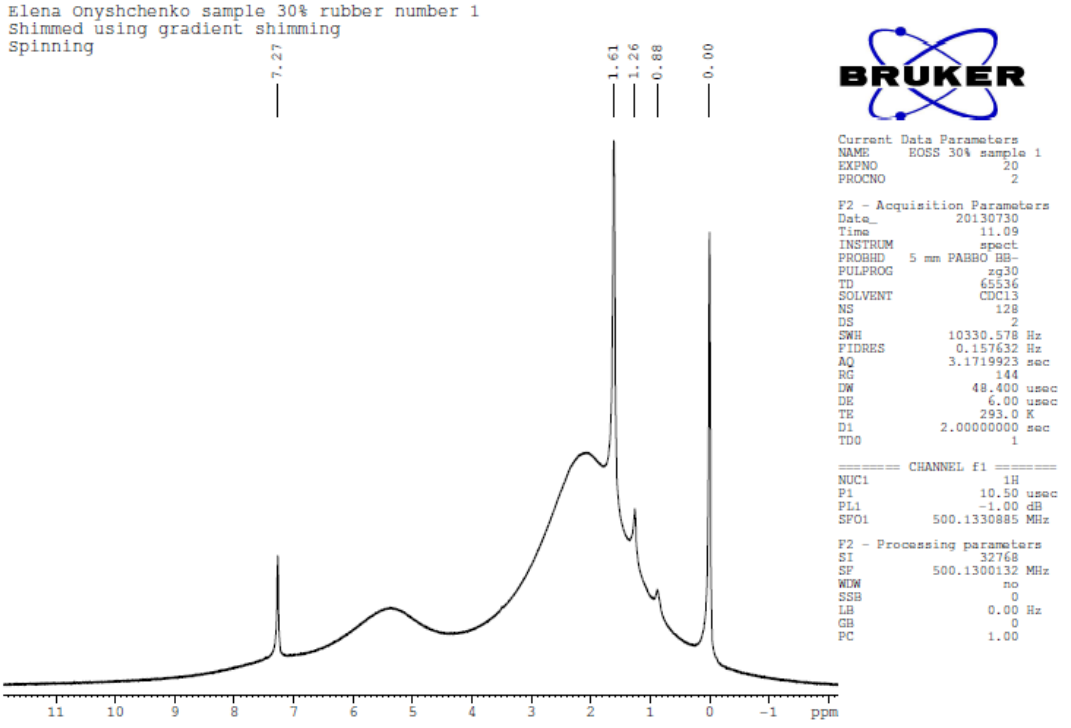


Fig. 4.15 NMR spectrum of 30% blend sample

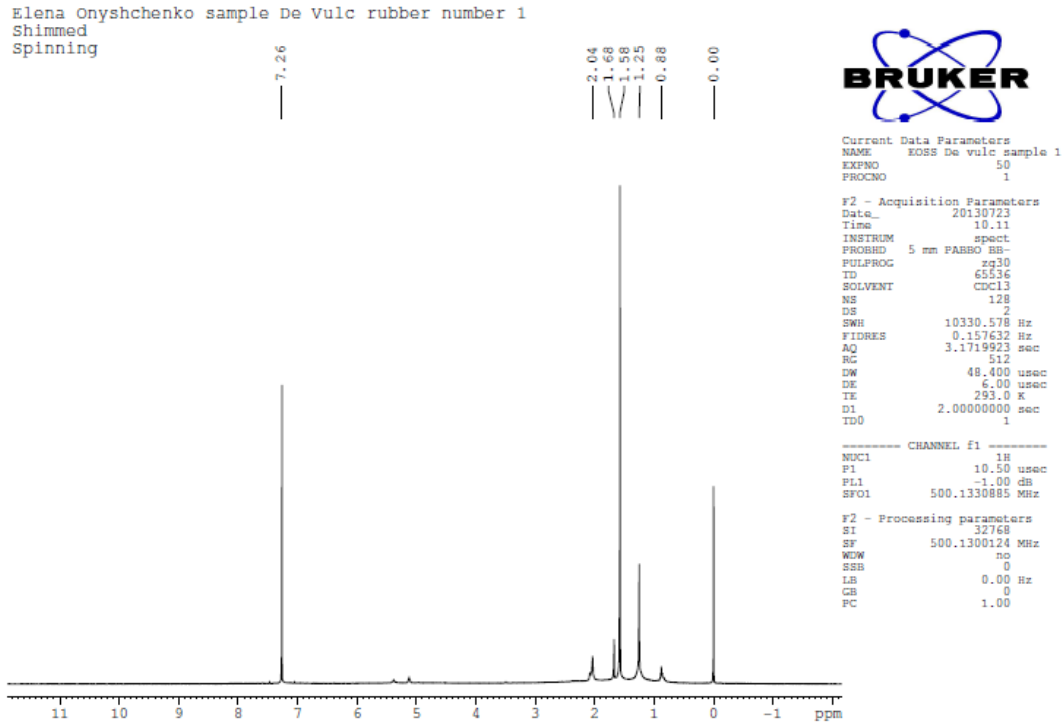


Fig.4.16 NMR spectrum of de-vulcanised rubber crumb extract

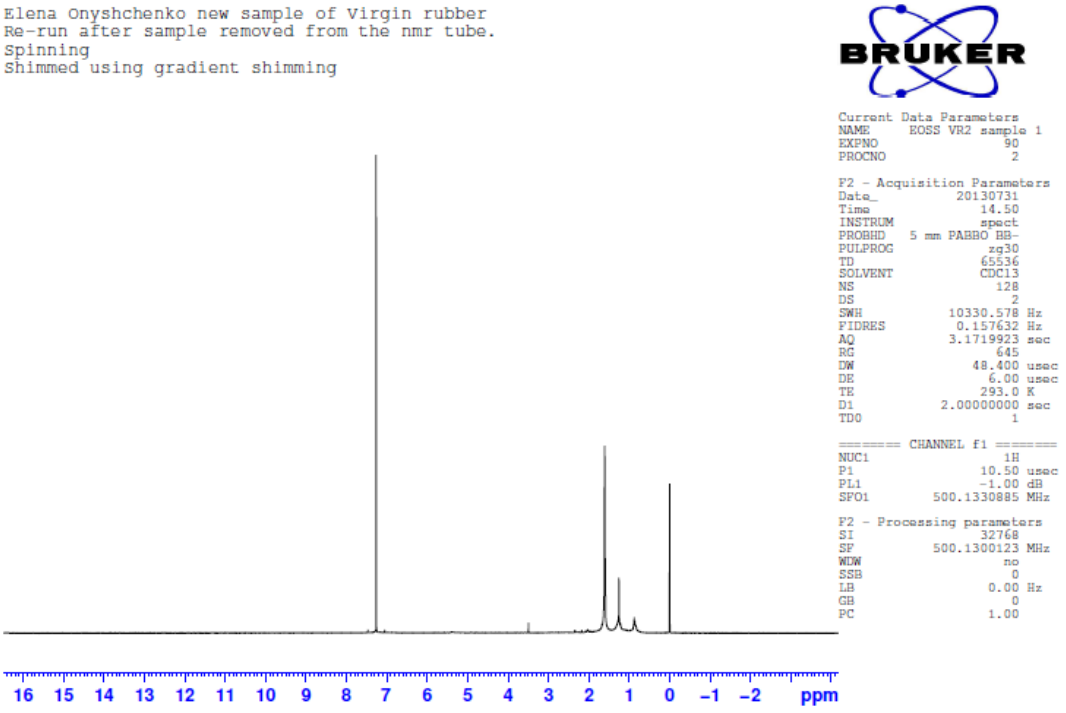


Fig.4.17 NMR spectrum of virgin rubber extract

4.7 Mechanical testing

Hardness

A hardness measurement is a simple way of obtaining a measure of the elastic modulus of rubber material which is related to CRD.

Sample preparation:

Three round samples from each compound (Table 4.1) were tested to determine its hardness. The samples were prepared by compression moulding (Daniel Electrical press at optimum curing conditions) and had the following dimensions: approx. 43.8 mm in diameter and 4.8 mm thick.

Procedure:

The procedure was carried out in accordance with BS ISO 48:2007 (Method N)[155] using a Wallace Dead Load Hardness tester, equipped with a ball indentor of 2.5 mm acting under a total force of 5.7 N. The results were expressed in International Rubber Hardness Degrees (IRHD). One measurement was made at three different points distributed over the test piece and the median value was recorded.

Compression set

Compressions set measurements are used to investigate the long term effects of an applied stress or strain. The measurement of set is a very effective quality control test as it is a relatively simple procedure and the results are sensitive to the state of cure. The testing procedure was carried out in accordance with standard[156] ISO 815- 1:2008.

Sample preparation:

Three samples from each rubber compound (Table 4.1) were tested. The compression set buttons were obtained by compression moulding (Daniel Electrical press at optimum curing conditions) and had the following dimensions: approx. 13.00 mm diameter and 6.3 mm thickness. The thickness of each sample was measured in the centre with the gauge specified in the standard.

Procedure:

The samples were lubricated on both sides with glycerine and placed in the compression apparatus. The apparatus consisted of four smooth, flat, highly polished plates between the two faces of which the test pieces were compressed by approx. 25% of the original thickness. The plates were bolted. The bolts were in the form of rings and 4.74 mm in thickness. The apparatus containing samples was placed in uniformly heated oven (3kW laboratory fan oven with temperature range 0 to 300^0 C) and held under a constant temperature of 120^0 C for 7 days. The temperature was checked at regular intervals to ensure adequate heating. After seven days, the apparatus was taken out of the oven and unbolted. The samples were taken out and placed on a clean wooden surface for 30 minutes and then their thickness was measured.

Expression of results

The compression set at constant strain is the difference between the original thickness of the test piece and that after recovery expressed as a percentage of the initially applied compression. It was calculated using the following equation:

$$\boldsymbol{Compression\ set} = \frac{\boldsymbol{t_0 - t_r}}{\boldsymbol{t_0 - t_s}}\ \boldsymbol{x\ 100\%} \qquad \textbf{(4.4)}$$

Where:

t_0 is the original thickness of test piece, mm

t_r is the thickness of test piece after recovery, mm

t_s is the thickness of the bolt

Tensile properties

Tensile stress/strain measurements are made in tension and provide a guide to the quality of the rubber as well as demonstrating how a rubber product may behave under tension. In this work, tensile properties of de-vulcanised tyre truck compound and blends were compared to the virgin material and related to other CRD related properties (e.g. rheological, vulcanisation, swelling). The tensile properties which were determined by this method included: the tensile strength, the elongation at break, the stress at a given strain and the elongation at a given strain.

Equipment:

Tinius Olsen Tensometer with QMat software

Samples:

Compression moulded tensile sheets (150mm X 150mm X 2mm) were produced from all samples (Table 4.1) at optimum curing conditions using a Daniel Electrical press set to 150^0C. Vulcanised sheets were left at room temperature for 24 hours prior to testing.

Procedure:

The tensile test procedure was carried out in accordance with standard[150] BS ISO 37:2005. Five dumb-bell shaped samples (75.5mm x 13mm) were stamped out from the vulcanised sheets such that the lengths of the samples were parallel to the direction of milling and their subsequent extension when under tension. The thickness of each sample was measured at its narrow (central) part. Three measurements were made and their mean value was used for calculation of the cross section area. The width of the sample was taken as the distance between the cutting edges of the die (4.5 mm).

A Tinius Olsen Tensometer coupled with QMat software was used for determination of tensile properties. The tensometer settings are included in Table 4.5. Five samples from each compound were tested and any samples which did not break within the central (narrow) portion were rejected.

Table 4.5 Tensometer settings for tensile test

Load Range	225 N
Preload	0
Cross-head Speed	500 mmmin^{-1}
Approach speed	0.001 mmmin^{-1}
Extension range	1500 mm
Initial grip separation	45 mm

Tear strength

The tear strength of filled NR compounds depends on the useful range of cross-link density and the types of cross-links[157]. The tear properties of vulcanised samples were determined in accordance with standard[158] BS ISO 34-1:2004. Method A, based on a trouser test piece, was employed in this work. This type of test piece was selected as it is not sensitive to the length of the cut. In addition, the results obtained by this method can be easily related to the fundamental tear properties (e.g. tear strength and tearing energy) and are less sensitive to modulus effects than in Method B or C. Furthermore, the rate of tear propagation can be directly related to the rate of grip separation.

Equipment:

Tinius Olsen Tensometer with QMat software

Samples:

Compression moulded tensile sheets (150mm X 150mm X 2mm) were produced from all samples at optimum curing conditions using a Daniel Electrical press set to 150^{0}C. Vulcanised sheets were left at room temperature for 24 hours prior to testing.

Procedure:

Specimens were cut from the vulcanised sheets using a standard cutting die for the trouser test piece. Each specimen, a thin rectangular piece, was then cut centrally along its legs (in the direction of milling) so two legs were formed as illustrated in Fig. 4.18. During the test the legs were pulled apart (Fig. 4.19) at a constant speed of 100 mm min^{-1} until the specimen was fully torn.

For every compound, five specimens were prepared. The thickness and width of the specimens were measured and recorded.

During the tear test, the type of failure for each compound was visually observed and the photographs of torn samples were taken to support discussion.

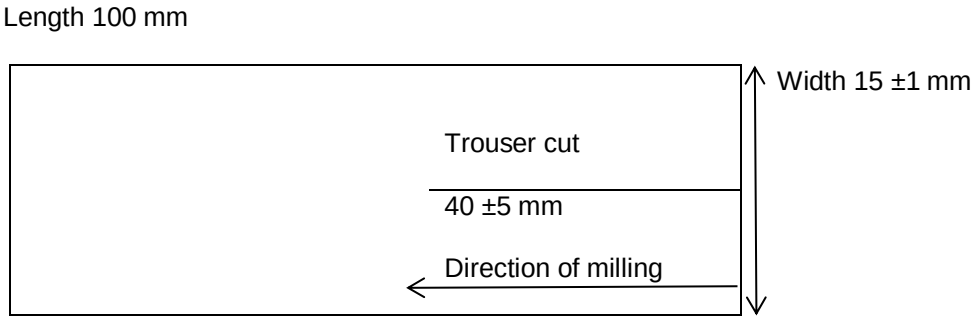


Figure 4.18 Trouser test specimen

Figure 4.19 Trouser test piece in a tensometer

Five trouser samples from each compound were subjected to a tearing test using a tensometer with the settings listed in Table 4.6 and the tear strength of each compound (mean value of 5 samples) was determined using QMat software as the median force to thickness ratio.

Table 4.6 Tensometer settings for tear test

Load Range	200 N
Preload	0
Cross-head Speed	100 mm min^{-1}
Extension range	1000 mm
Initial grip separation	50 mm

Tearing behaviour

The tear strength parameter that can be readily obtained by this standard method is the force per unit thickness (N/mm) required to tear a rubber sample of a specified geometry. The limitations of using this parameter to characterise the tearing behaviour of rubber are its strong dependence on the type of test piece employed (e.g. crescent, angle or trouser) and the speed of stretching and

the temperature. However, this parameter can be readily obtained under standard conditions and therefore, provide a useful comparison of de-vulcanised materials and blends during the development stage and for the purpose of quality control. It has to be noted however, that a more fundamental characteristic of the tearing strength of rubbers is the *tearing energy,* best defined as the energy required to create new surfaces by tearing[159]. As the tearing energy is independent of the form of the test piece it is considered to be the "true" characteristic of the material[160]. However, the many different practical approaches outlined below available to determine this parameter, combined with limited information on the test conditions used, make the tearing energy results less suitable for the initial comparisons planned for this research work.

The tearing energy concept was first developed by Rivlin and Thomas[161] who formulated two main criteria for tearing of a cut or notched elastic test piece independent of its shape:

1) The critical stress criterion: the cut will spread when the stress at its tip reaches a critical value
2) Elastic energy density criterion, originally suggested by Griffith[162]: a cut of length c will spread by an amount dc at a certain overall deformation of the test-piece , if the energy W stored elastically in the test-piece is thereby decreased by an amount dW greater than the increase of surface free-energy due to the formation of new surface

Based on the above criteria Rivlin and Thomas devised a number of tests to experimentally determine the "critical tearing energy" in unfilled NR in terms of applied forces and displacements. However, in conventional tearing measurement, the magnitude of tearing energy is not only affected by test conditions (the rate and temperature of the test) but also by the types of failure: steady (smooth), stick-slip and knotty tearing[163–165]. During unstable tearing (stick-slip and knotty tearing) the tear does not propagate at a steady rate but arrests and reinitiates at relatively regular intervals, making experimental determination of critical tearing energy complex. To overcome this problem, Gent and Henry[166] developed a constrained trouser test piece by bonding thin metal shims on opposite sides of the specimen legs. However, even in the case of the constrained trouser test piece the development of unstable tearing is often not supressed substantially[167]. The origin of unstable tearing has been studied by De and Gent[157] who concluded that this type of behaviour is commonly observed in reinforced elastomers and is strongly dependent on the type of carbon black and elastomer used. Application of the "energetics approach" to solve the fracture problems in rubbers (e.g. small scale crack growth and fatigue, ozone attack, abrasion and cutting by sharp objects) has been further developed by Lake and co-workers[159,168,169]. Their approach was based on "limiting tearing energy" to the point below which no crack propagation occurs, and related to the molecular structure and chemical bond strength of vulcanised rubber. As the tearing mechanism in elastomers is highly complex it still remains a subject of advanced research[170].

Chapter 5: Results & Discussions

5.1 Mooney viscosity and Mooney relaxation

The Mooney viscosity of an unvulcanised rubber compound provides valuable information on its quality and processability. This section is therefore dedicated to the presentation and evaluation of the results of Mooney viscosity and Mooney relaxation measurements of the de-vulcanised and virgin materials and their blends for three different rubber products. In addition, the results were compared to establish their usefulness in indicating the efficiency of the de-vulcanisation process. Furthermore, the Mooney relaxation data (not currently applied in de-vulcanisation studies) was analysed and the most effective parameters (e.g. the rate of relaxation, percentage of Mooney torque retained at 30 seconds after stopping the rotor) have been proposed for consideration as more accurate indicative characteristics of the de-vulcanisation process.

Although, the closed-loop tyre material was the main focus of this research, two other products were also considered in this section. This was due to the reasons explained in Chapter 4, including the limited shelf life of the de-vulcanised materials and the inability to reproduce the rubber materials, generated as part of the *ReMould* project (a one off commercial trial). As the decision to use the Mooney relaxation measurement was made after the initial evaluation of the Mooney viscosity results, the clothing tape NR-based compounds and automotive weather strip EPDM-based compounds, produced towards the end of the *ReMould* project, were used to evaluate the Mooney relaxation test.

5.1.1 Mooney viscosity

Mooney viscosity measurements were carried out using the procedure described in section 4.2: Mooney viscosity and Mooney relaxation (Chapter 4). The results are presented in Tables 5.1 to 5.3 and Fig. 5.1.

Closed-loop tyre compounds

Detailed composition of the closed-loop tyre compounds is provided in Table 4.1 (Chapter 4).

As the Mooney viscosity relates to the modulus, the removal of cross-links during de-vulcanisation is expected to bring about a reduction in modulus and viscosity value[40]. The value of the Mooney viscosity of 100% de-vulcanised material (sample 8, Table 5.1) was high (121MU) and almost 12 times the value of the virgin material, leading to an indication of partial rather than full de-vulcanisation. High Mooney viscosity values (up to 157 MU) have also been reported[43] by the Tun Abdul Razak Research Centre where a small rotor was employed to determine the Mooney viscosities of pure de-vulcanisates for similar material (de-vulcanised waste truck rubber crumb). In practice, the de-vulcanised material will be blended with virgin compound to improve its quality and processability.

Consideration of the Mooney viscosity results for the closed-loop tyre blends (samples 2 to 7, Table 5.1) revealed a relatively low mean value (7±1 MU) of the blends that is comparable with the value for virgin material (10 MU). As low viscosity leads to better processability, these results indicate improved quality and processability of the blends compared to pure de-vulcanisate. Despite some fluctuations, the Mooney viscosity results of the blends did not show any clear trend between *changes in viscosity and increased amounts of de-vulcanised material* and the observed variation in the results for the blends (up to 14% of the mean) is likely to be related to changes in processing conditions or the materials' composition (e.g additives).

Table 5.1 Mooney viscosity results for the closed-loop tyre compounds

Sample: Closed-loop tyre	**Description**	**Mooney viscosity (Mooney Units, MU) MS (1+4) 100^{0}C** i	ii	iii	Average
1	Virgin rubber	10.5	10.5	10.0	10.3
2	5% blend	7.0	7.0	6.5	6.8
3	10% blend	5.5	5.5	6.0	5.7
4	15% blend	9.0	8.0	8.0	8.3
5	20% blend	6.5	7.0	6.5	6.7
6	25% blend	10	9.5	9.5	9.7
7	30% blend	7.0	7.5	7.0	7.2
8	DeVulCO"2 rubber crumb	121.0	120.0	121.0	120.7

Closing tape compounds

Table 5.2 Mooney viscosity results for the clothing tape (NR-based) compounds

Sample: NR	**Description**	**Mooney viscosity (MU) MS (1+4) 100^{0}C** i	ii	iii	Average
1	Virgin rubber	65.0	70.0	71.0	68.7
2	15% blend	75.0	73.0	73.0	73.7
3	25% blend	87.0	87.0	87.0	87.0

Samples 2 and 3 in Table 5.2 were blends of virgin clothing tape rubber with the addition of 15% and 25% respectively of the de-vulcanised waste clothing tape crumb as illustrated in Fig. 4.1 (Chapter 4).

The Mooney viscosity results of the clothing tape compounds (Table 5.2 and Fig. 5.1) showed the expected increase in viscosity following the addition of de-vulcanised material (sample 1 to sample 2: approx. 7% increase) and a further increase in viscosity value (sample 2 to sample 3: 1.5 % increase) with a higher level of de-vulcanised material. A sample of pure de-vulcanisate was not available for testing.

Automotive weather strip compounds

Table 5.3 Mooney viscosity results for the automotive strip (EPDM-based) compounds

Sample: EPDM	**Description**	**Mooney viscosity (MU) MS (1+4) 100^{0}C**			
		i	ii	iii	Average
1	Virgin rubber	83.0	84.5	83.5	83.7
2	15% blend	96.5	94.5	97.5	96.1
3	25% blend	104.0	99.5	105.0	102.8
4	35% blend	99.0	98.0	99.0	98.7
5	DeVulCO”2 rubber crumb	190.0	189.0	189.5	189.5

Samples 2, 3 and 4 in the Table 5.3 were blends of virgin automotive weather strip rubber with the addition of 15%, 25% and 35% respectively of de-vulcanised waste automotive strip crumb as illustrated in Fig. 4.1 (Chapter 4).

The Mooney viscosity results of the automotive strip compounds (Table 5.3 and Fig. 5.1) showed a similar trend to the clothing tape compounds with the exception of sample 4 that had a slightly lower viscosity than sample 3. However, the increase in Mooney viscosity in corresponding blends was generally higher for the automotive strip material (there was an increase of 13% from sample 1 to sample 2 and a 6.5% increase from sample 2 to sample 3) than for the clothing tape . In addition, the difference in Mooney viscosity between de-vulcanised and virgin material was approximately 6 times less in the case of the automotive strip compounds as compared to the closed-loop tyre materials.

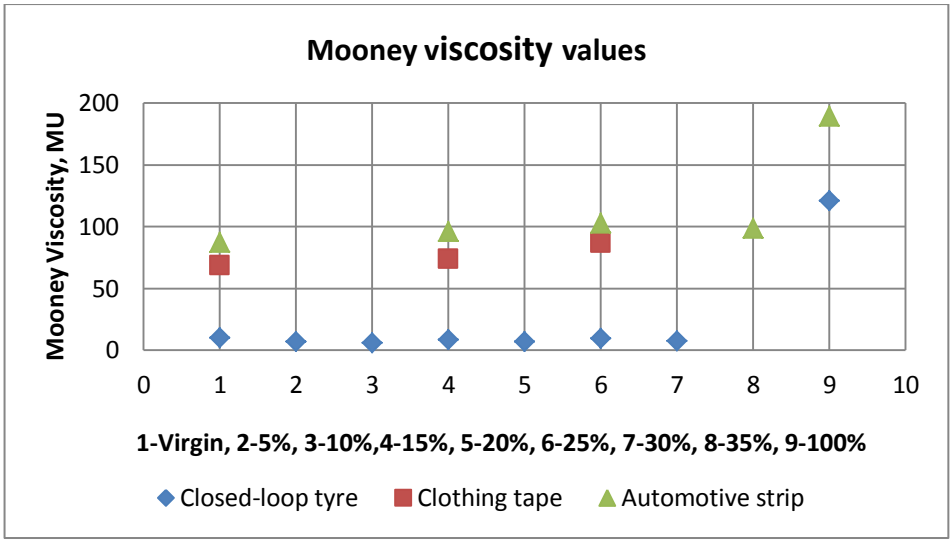


Fig.5.1 Comparative results of the Mooney viscosity for three different materials

Overall the following conclusions have been made:

- The difference in the viscosities between the three different products is due to the difference in their compound formulations
- The final Mooney viscosity of the closed-loop tyre de-vulcanisate is high and the material needs to be blended with virgin rubber to improve its quality and processability. However, the Mooney viscosities of the blends were low and comparable to the value of virgin material. This could be attributed to the dominant role of the virgin material in the blends or the use of additives known to reduce viscosity (e.g NR) during blending
- The Mooney viscosities of the automotive weather strip blends and clothing tape blends were higher than for the corresponding virgin material. Furthermore the increased loading of de-vulcanised material in the blends led to increased viscosity that could be attributed to the restriction of the flow caused by partially cross-linked crumb. It has been reported[171] that highly aggregated tyre waste powder is capable of trapping the matrix into its void space, leading to increased effective volume of waste rubber and hence, increased viscosity of the blends.

To sum up, as the value of Mooney viscosity can be significantly influenced by processing conditions and additives, it should be considered alongside additional, “non-standard” parameters (e.g the Mooney relaxation test) to more reliably indicate the efficiency of the de-vulcanisation process.

5.1.2 Mooney Relaxation

Mooney relaxation measurements were carried out using the procedure described in section 4.2: Mooney viscosity and Mooney relaxation (Chapter 4). The results of the test are presented in Tables 5.4 to 5.7 and Figures 5.2 to 5.13.

Table 5.4 Mooney viscosity and Mooney relaxation results for the clothing tape (NR-based) compounds

Sample: NR	Description	Max torque, (MU)	MV, (MU)	Constant k (MU)	slope α	α+1	$M_{ret.30s}$ (%)
1	Virgin	88.0	68.7	64.0	-0.52	0.48	17.0
2	15% blend	83.3	73.7	68.7	-0.53	0.47	16.7
3	25% blend	100.0	87.0	84.0	-0.45	0.55	22.2

The parameters in Table 5.4 and Table 5.5 have the following meanings:

Maximum torque, expressed in Mooney units, is the torque at the start of the measurement, after the initial preheating time of 1 minute,

Mooney viscosity (MV) or the final Mooney viscosity, expressed in Mooney units, is the torque at 5 minutes (1 minute – preheat time followed by 4 minutes of test time or MS (1+4) 100^0C),

Constant k, expressed in Mooney units is the constant (equation 1, Chapter 3) equal to torque at 1 second after the rotor is stopped,

α is the rate of the stress relaxation (the slope of the relaxation function)

(α +1) is the Mooney elasticity parameter,

$M_{ret.30s}$, is the percent Mooney torque retained at 30 seconds after stopping the rotor[172].

$$M_{ret.30s} = \frac{RT\ at\ 30s}{MV}\ x\ 100\% \qquad (5.1)$$

Where:

RT at 30 s is the Relaxation torque at 30 seconds after the rotor is stopped and

MV is the final Mooney viscosity: MS (1+4) 100^0C

Table 5.5 Mooney viscosity and Mooney relaxation results for the automotive strip (EPDM-based) compounds

Sample: EPDM	Description	Max torque, (MU)	MV, (MU)	Constant k (MU)	slope α	α+1	$M_{ret.30s}$ (%)
1	Virgin	114.6	83.7	75.3	-0.36	0.64	22.0
2	15% blend	142.8	96.1	87.0	-0.28	0.72	30.5
3	25% blend	152.7	102.8	90.0	-0.26	0.74	31.4
4	35% blend	175.7	98.7	92.0	-0.25	0.75	34.8
5	DeVulCO"2 rubber crumb	318.0	189.5	184.5	-0.14	0.86	56.5

Fig. 5.2 and Fig. 5.3 represent the combined data for the Mooney viscosity and Mooney relaxation test. The highest points of the torque represent the maximum torque, the next set of points represent the final Mooney viscosity values or MV and the third set of points represent the Mooney relaxation torque at 1 second after the rotor stopped. The rest of the points correspond to the Mooney relaxation torque, measured every 10 seconds until the plateau was reached.

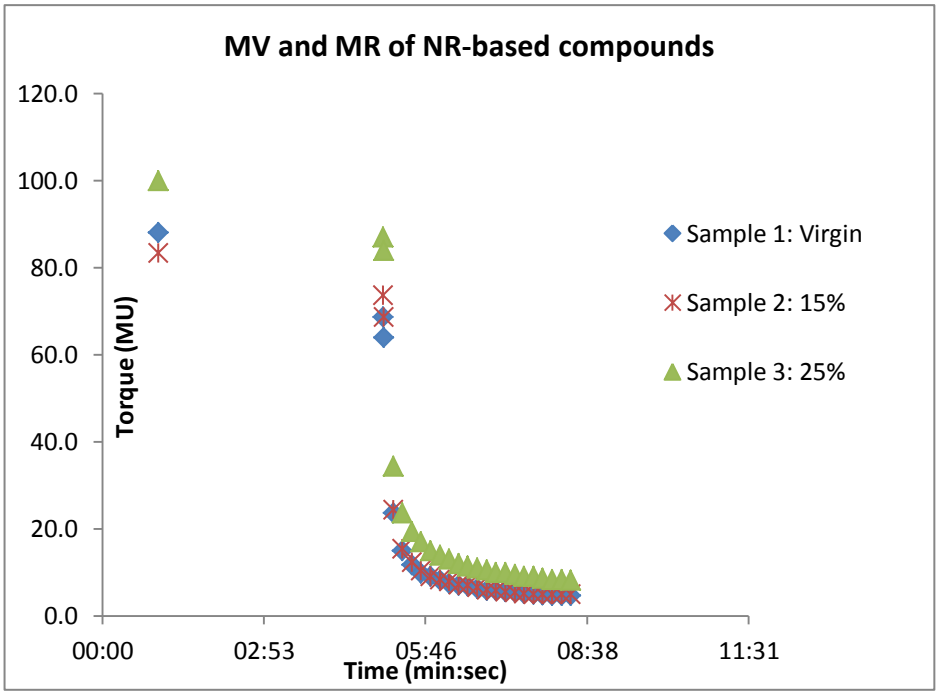


Fig.5.2 Mooney viscosity and Mooney relaxation for the clothing tape NR-based compounds

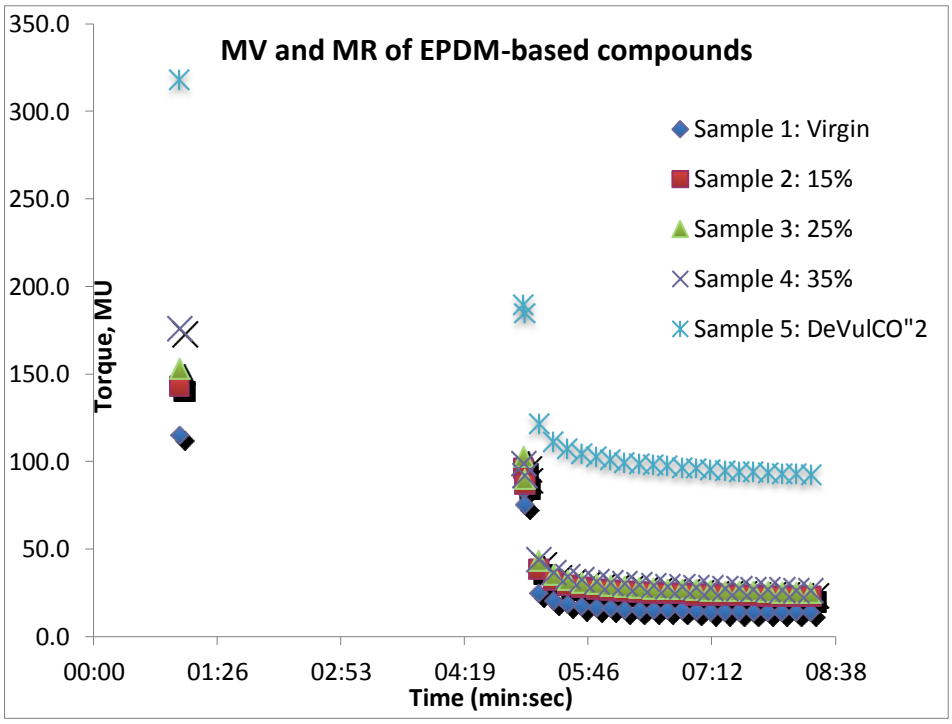


Fig.5.3 Mooney viscosity and Mooney relaxation for automotive strip EPDM-based compounds

Consideration of the Mooney relaxation parameters

Mooney viscosity is related to the viscoelastic behaviour of material, while the Mooney relaxation data distinguishes between the elastic and viscous components and hence, offers more accurate and independent information on elasticity.

Furthermore, individual relaxation parameters were analysed to determine their potential to describe the elastic component of the material as a means for evaluating the de-vulcanisation process.

Constant k

Constant k, does not change with time for the same material and is recorded at the beginning of the Mooney relaxation test, 1 second after the rotor is stopped. This parameter has been reported by Malac[82] to be in close correlation with the final Mooney viscosity value, showing a linear relationship with a high correlation coefficient *(R^2=0.9821)* when applied to different grades of raw NR. This is not surprising as the 1 second difference in the timing of the measurements is not sufficient for any difference in relaxation rate to have a significant effect on the change in torque, suggesting that constant k should provide similar information on rubber processability and viscoelastic behaviour as Mooney viscosity.

Fig. 5.4 is based on the results of the clothing tape NR-based compounds (sample description is in Table 5.3) and is consistent with results observed by Malac, showing a linear relationship between the constant k and Mooney viscosity with a high correlation coefficient (*R^2 = to 0.9982)*.

A high correlation coefficient *(R^2=0.9972)* is also evident from Fig. 5.5 which is based on the results of the automotive weather strip compounds. In fact, the Mooney viscosity and constant k data for both the NR and EPDM compounds fit well together (R^2=0.9932).

Overall, the following trend has been observed in relation to constant k:

- linear correlation exists between the constant k and Mooney viscosity, with high correlation coefficients as illustrated in Fig. 5.4 and Fig. 5.5, showing an increase in constant k with an increase in Mooney viscosity.
- the highest constant k and hence, Mooney viscosity were observed in case of the pure de-vulcanisate (sample 5, Fig. 5.5).
- Constant k increased with the addition of de-vulcanised material (blends), with higher additions leading to a higher value of k (samples 2 to 3 in Fig. 5.4 and samples 2 to 3 and 3 to 4 in Fig. 5.5).

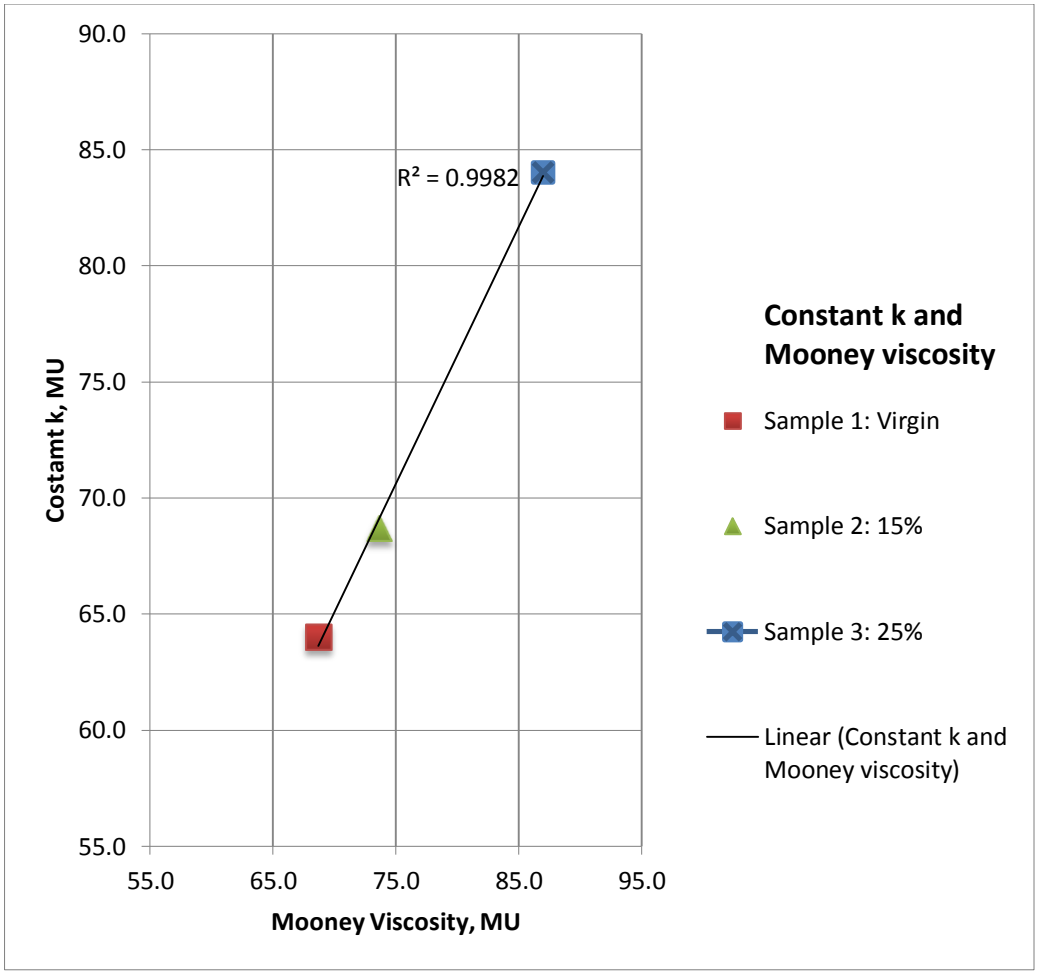


Fig.5.4 Constant k and Mooney viscosity for clothing tape NR-based compounds

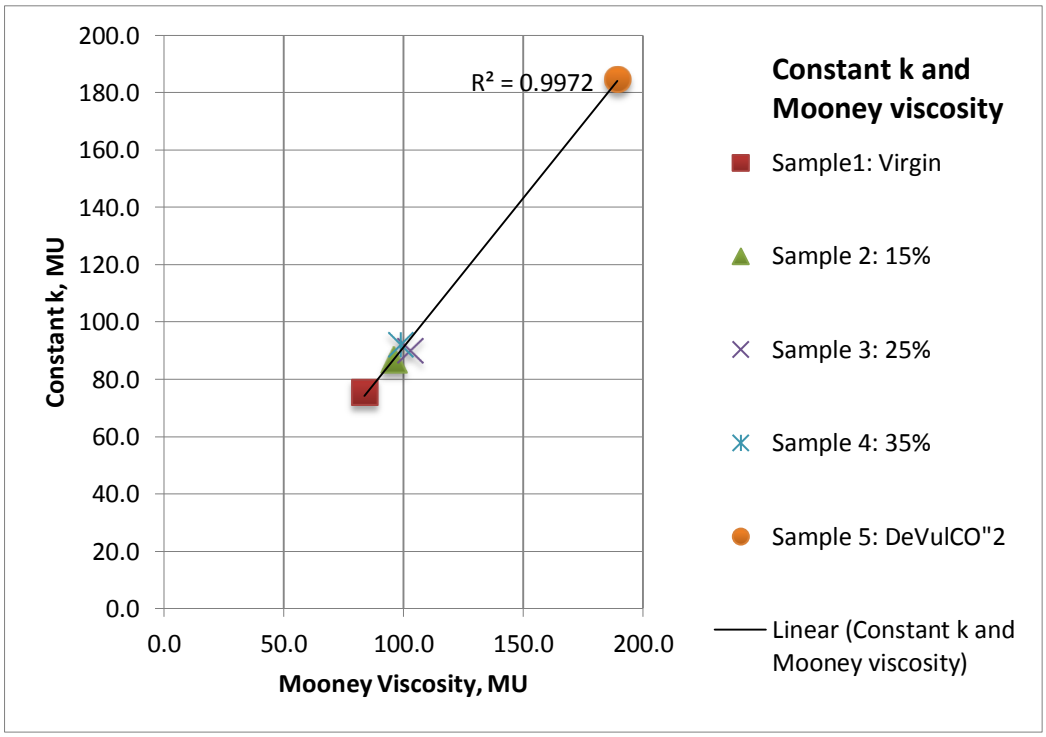


Fig.5.5 Constant k and Mooney viscosity for automotive strip EPDM-based compounds

Rate of relaxation, α

As explained earlier, unvulcanised rubber material is not fully viscous but has an elastic component of deformation. The rate of relaxation, *α* in equation 1 (Chapter 3) is a measure of the speed of relaxation and provides information on the elastic behaviour of rubber material. Therefore, the rate of relaxation can be considered as a measure of the intrinsic elasticity of the material[82].

In relation to de-vulcanised rubber materials and their blends with a corresponding virgin compound, this parameter can provide a valuable insight into the efficiency of the de-vulcanisation process. It is logical to assume, that retained de-vulcanised rubber crosslinks may contribute to an overall elastic response and lead to a higher *α* value in the de-vulcanised compound than its blends with virgin material.

The rate of relaxation can be determined by converting equation 1 ($M = kt^{a}$) into equation 2 ($\log(M) = a\ log(t) + \log(k)$) and performing the following re-arrangements in relation to *α*:

$$\boldsymbol{a\log(t) = \log(M) - log(k)} \qquad \textbf{(5.2)}$$

Hence,

$$\boldsymbol{a = \frac{\log(M) - log(k)}{\log(t)}} \quad or \qquad \textbf{(5.3)}$$

$$\boldsymbol{a = \frac{\log\left(\frac{M}{k}\right)}{\log(t)}} \qquad \textbf{(5.4)}$$

In practice the rate of relaxation is usually determined by plotting values of log(M) against log(t) for the relevant relaxation data. In this case, the graph yields the rate of relaxation (the slope of the graph), in addition to the intercept k.

The log-log plots for the clothing tape NR-based compounds and automotive strip EPDM-based compounds are presented in Fig.5.6 and Fig.5.7. On the graphs, the highest value of the torque, log(MU) for each material corresponds to the torque at 1s after the rotor is stopped (constant *k*) and the rest of the points – to the torque values taken continuously every 10 seconds until the plateau was reached. Hence, in this study the rate of relaxation, α for each material was taken as the slope of the relevant graph.

It was observed that a sharp drop in Mooney relaxation torque was evident in the first 30 seconds after the rotor has stopped, followed by the gradual linear decrease in Mooney relaxation torque within the next 60 seconds until a plateau was reached.

The results of the Mooney relaxation test were found to conform well to the power law equation $M = kt^{a}$ (equation 1, Chapter 3) as evident from the high correlation coefficients for all materials in Fig. 5.6 and Fig. 5.7.

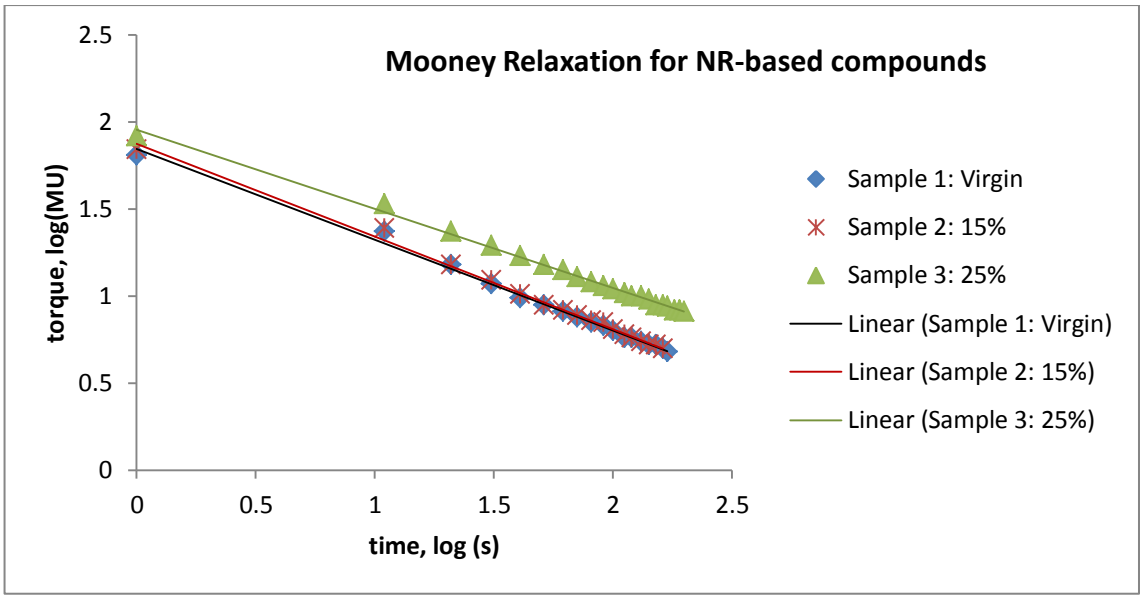


Fig.5.6 Mooney relaxation in a log-log plot for the clothing tape NR-based compounds (Sample 1: R^2= 0.9950; Sample 2: R^2=0.9950; Sample 3: R^2=0.9962)

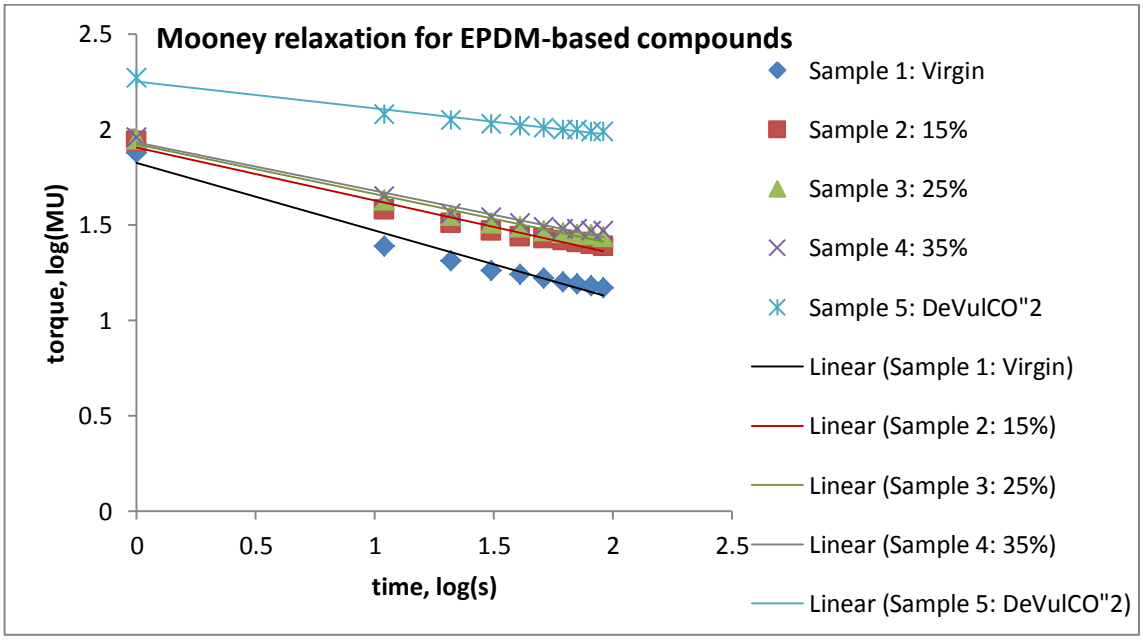


Fig.5.7 Mooney relaxation in a log-log plot for the automotive strip EPDM-based compounds (Sample 1: R^2= 0.9650; Sample 2: R^2=0.9753; Sample 3: R^2=0.9799; Sample 4: R^2=0.9757; Sample 5: R^2=0.9732)

It is apparent from plots in Fig. 5.6 to 5.7 and Tables 5.4 to 5.5 that the rate of relaxation (slope α) is increasing with the addition of de-vulcanised material (except for sample 2, clothing tape compound) with the highest value attributed to 100% de-vulcanised material. As a steep slope corresponds to less uncured elasticity, the results indicate an increase in elasticity with the addition of de-vulcanised material and this can be related to the remaining cross-links in the structure.

Mooney elasticity parameter: α+1

Mooney elasticity or ***(α+1)*** was proposed by Malac[82] as an alternative to ***α*** to aid interpretation of negative results by turning them into positive values: with a higher value of (α+1) related to a higher elasticity component in a material.

It can be seen from Table 5.4 and Table 5.5 that the values of the Mooney elasticity parameter is increasing (except sample 2 clothing tape compound), with higher values attributed to blends with higher amount of de-vulcanisate. The highest value of the Mooney elasticity parameter was observed for the de-vulcanisate (sample 5, automotive strip compound). This indicates a higher elasticity component in blends and de-vulcanisate compared to the virgin material. These results can be explained by the presence of some remaining cross-link in the structure of de-vulcanised material, contributing to the overall elastic component and can be used as an indication of the de-vulcanisation efficiency.

Percent Mooney retention torque, $M_{ret.30s}$

It has been noted by Bristow et al[173] that the rate of relaxation can be susceptible to timing errors, with an error of even 1 second having a significant impact on the relaxation rate value. It has also been observed during this study, that the value of the rate of relaxation, taken as a slope, can differ from the value calculated (equation 5.4) at each single point across the relaxation period. Therefore, other "non-standard" parameters have been considered alongside the rate of relaxation to characterise the Mooney relaxation behaviour of the de-vulcanised rubber materials. One of these parameters is the percent Mooney torque, retained after a specified period of relaxation.

Percent Mooney torque retained at 30 seconds after stopping the rotor is a stress relaxation parameter[172] that relates the Mooney relaxation torque at 30 seconds after stopping the rotor to the final Mooney viscosity value. The current set of results suggests that this parameter could be particularly important because of its association with the start of the more gradual decrease of the Mooney relaxation torque with time on a log-log plot (Fig.5.6 and Fig. 5.7). The results of $\boldsymbol{M_{ret.30s}}$ for both products (Table 5.4 and Table 5.5) show a trend similar to the results of ***α*** and ***(α+1)*** and confirm usefulness of this parameter for characterisation purposes.

Percent Mooney torque retained at other relaxation times has also been considered for comparison purposes. Using the same approach as with $M_{ret.30s}$ (equation 5.1) the results of percent Mooney torque retained at 10, 20, 50 and 90 seconds for both the NR and EPDM compounds were determined (Fig. 5.8 and Fig. 5.9). All results show similar trend and decrease with time. However, the values obtained at 30 seconds seem to indicate the start of the more gradual decrease in Mooney retention torque, avoiding drawbacks with using early (no significant change) or late (plateau) time of relaxation.

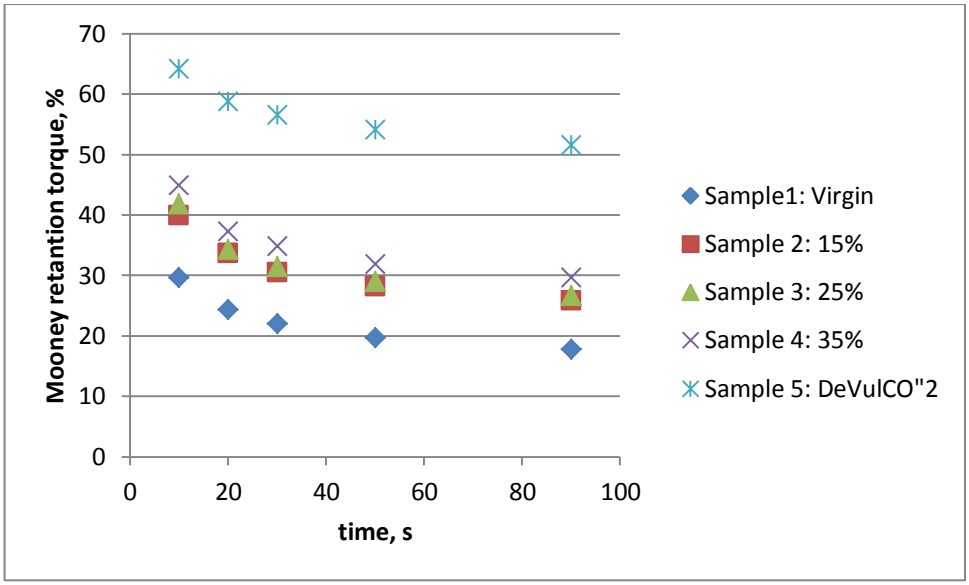


Fig. 5.8 Mooney retention torque at 10, 20, 30, 50 and 90 seconds for EPDM compounds

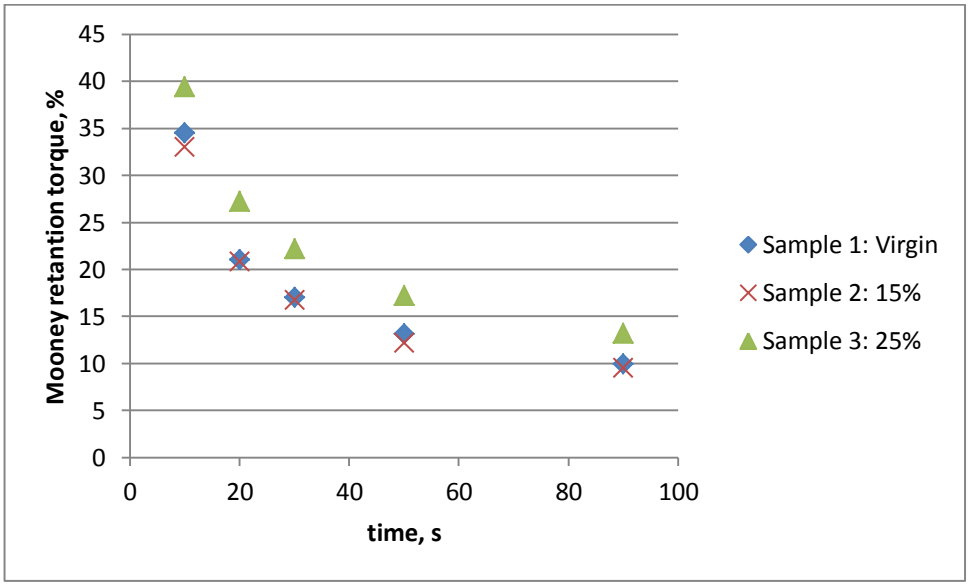


Fig. 5.9 Mooney retention torque at 10, 20, 30, 50 and 90 seconds for NR compounds

Change in torque after fixed times of relaxation

Additional relaxation parameters, D_{20} and D_{90} (equations 5.5-5.6), based on the difference in Mooney viscosity and relaxation torque at 20s and 90s seconds respectively, originally proposed by Bristow et al[173] to study the processability of NR, have also been analysed.

$$D_{20} = MV - RT \; at \; 20s \qquad (5.5)$$

$$D_{90} = MV - RT \; at \; 90s \qquad (5.6)$$

Where:

RT at 20 s is the Relaxation torque at 20 seconds after the rotor is stopped,
RT at 90 s is the Relaxation torque at 90 seconds after the rotor is stopped and
MV is the final Mooney viscosity: MS (1+4) 100^0C

Their results (Fig. 5.10 and Fig. 5.11) showed a similar trend to the Mooney viscosity results but did not follow the pattern observed with the percent Mooney torque retained at a specified relaxation time (e.g $M_{ret.30s}$).

Correlation of the selected Mooney relaxation parameters

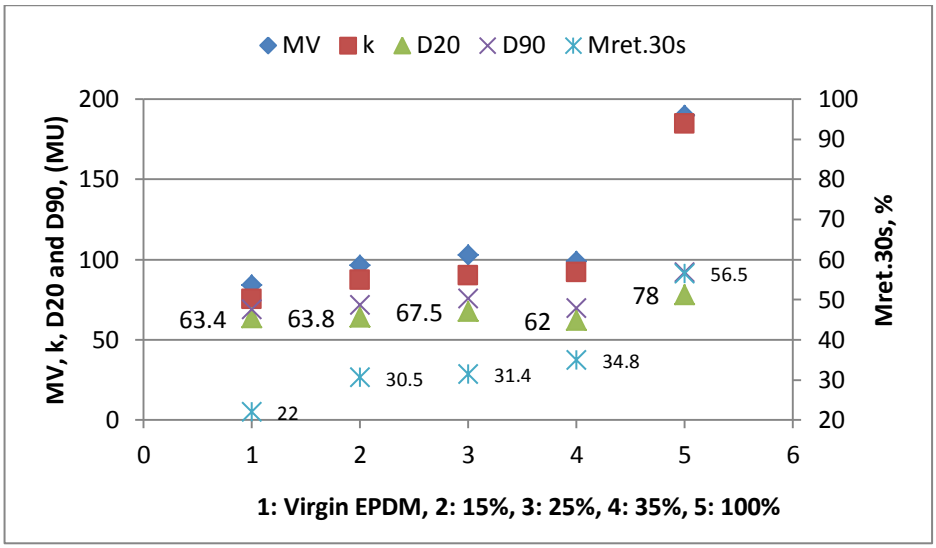


Fig. 5.10 Comparison of selected Mooney relaxation parameters and MV for EPDM compounds

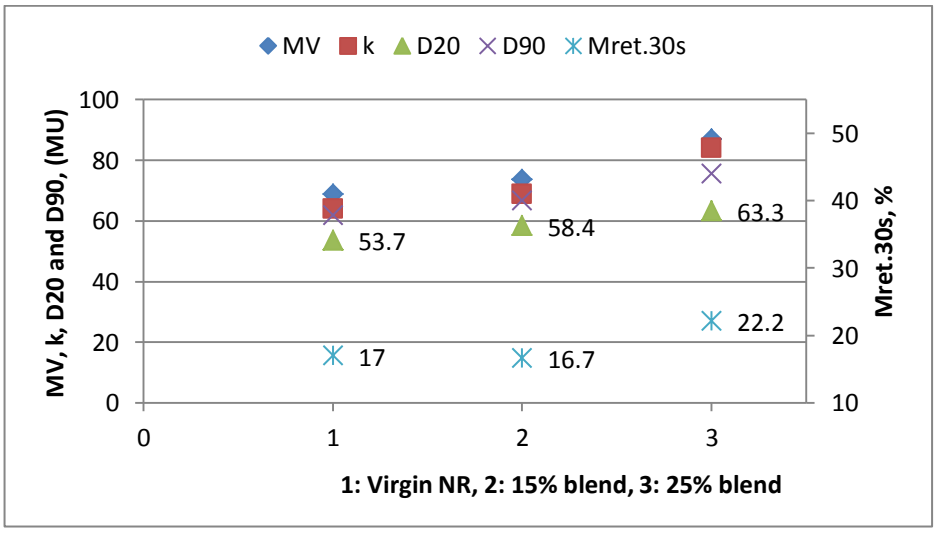


Fig. 5.11 Comparison of selected Mooney relaxation parameters and MV for NR compounds

Comparison of the selected Mooney relaxation parameters (Fig. 5.10 and Fig. 5.11) showed a good correlation between Mooney Viscosity and the following relaxation parameters:

- k

- D_{90}
- D_{20}

As parameter k showed the highest correlation coefficient for both the NR and EPDM compounds, it can be considered for use alongside MV to characterise the viscoelastic behaviour of material. Both, D_{90} and D_{20} can be useful in providing additional information on relaxation behaviour when comparing different compounds, but they do not agree with the $M_{ret.30s}$ results. However, the results in Fig. 5.12 and Fig. 5.14 show good agreement between the rate of relaxation and $M_{ret.30s}$. Moreover, further analysis of the selected Mooney relaxation parameters (Fig. 5.13 and Fig. 5.15) revealed a high linear correlation between the rate of relaxation and $M_{ret.30s}$, particularly in case of EPDM material.

The results of the most significant Mooney relaxation parameters are presented in Table 5.6 and 5.7.

Table 5.6 Comparative results of the Mooney relaxation parameters for the automotive strip EPDM-based compounds

Sample EPDM	**Description**	**Rate of relaxation, slope α**	**Elasticity parameter,** (α+1)	**$M_{ret.30s}$, %**	**Constant k, (MU)**
1	Virgin rubber	-0.36	0.64	22.0	75.3
2	15% blend	-0.28	0.72	30.5	87.0
3	25% blend	-0.26	0.74	31.4	90.0
4	35% blend	-0.25	0.75	34.8	92.0
5	DeVulCO”2 rubber crumb	-0.14	0.86	56.5	184.5

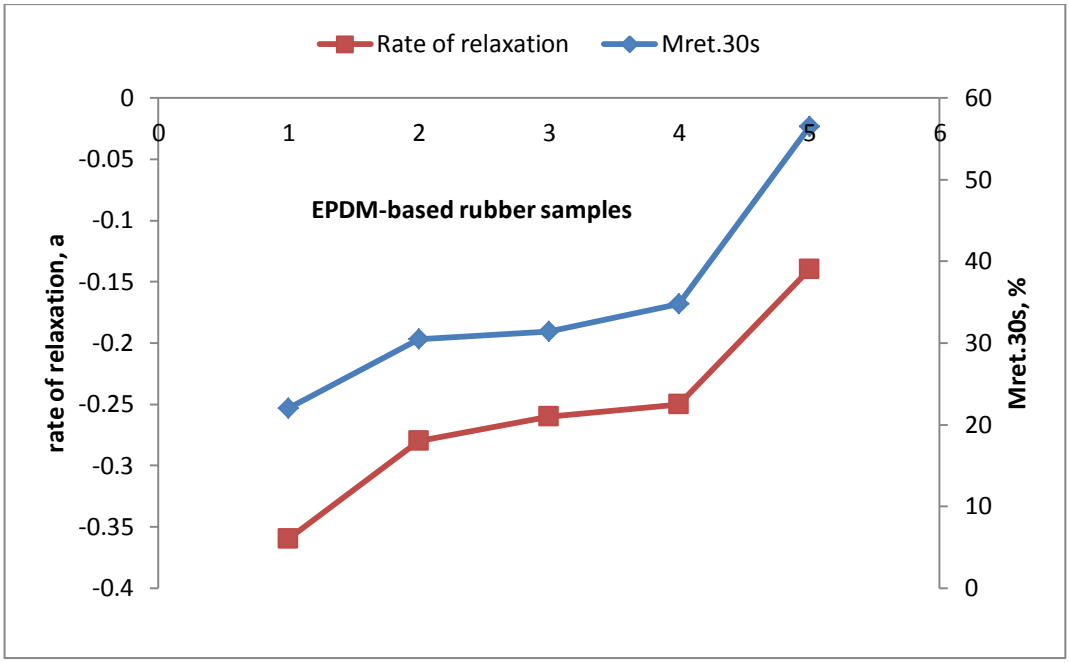


Fig. 5.12 Rate of relaxation and percent Mooney torque retained at 30s after the rotor is stopped for the automotive strip compounds

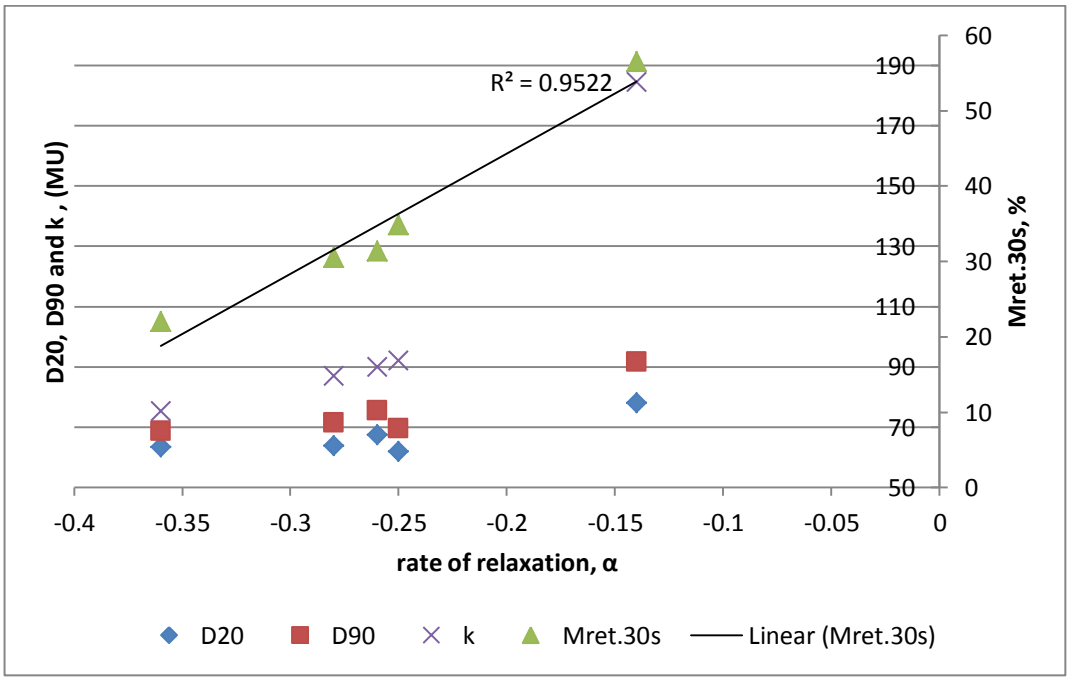


Fig. 5.13 Correlation between the rate of relaxation and selected Mooney relaxation parameters for the automotive strip compounds

Table5.7 Comparative results of the Mooney relaxation parameters for the clothing tape NR-based compounds

Sample NR	Description	Rate of relaxation, α	Elasticity parameter, (α+1)	$M_{ret.30s}$, %	Constant k, (MU)
1	Virgin rubber	-0.52	0.48	17.0	64.0
2	15% blend	-0.53	0.47	16.7	68.7
3	25% blend	-0.45	0.55	22.2	84.0

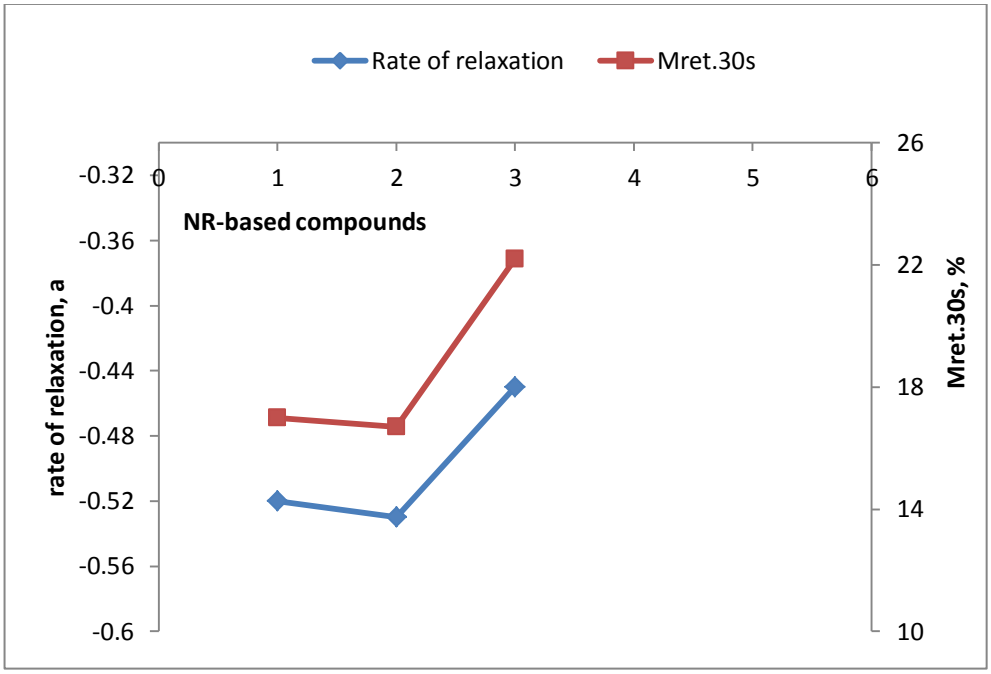


Fig. 5.14 Rate of relaxation and percent Mooney torque retained at 30s after the rotor is stopped for the clothing tape compounds (sample description in Table 5.4)

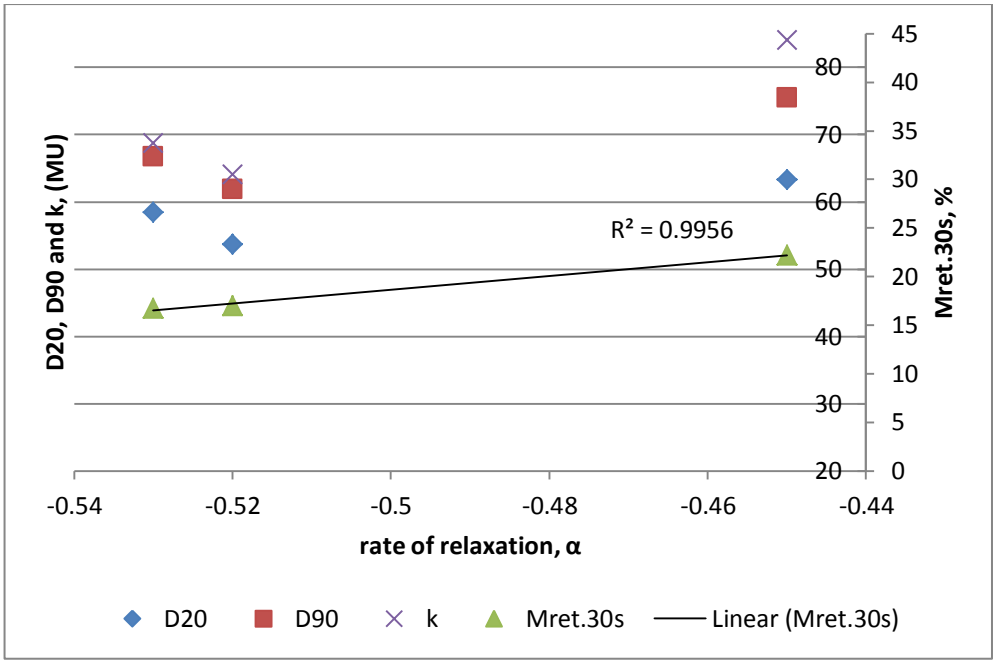


Fig. 5.15 Correlation between the rate of relaxation and selected Mooney relaxation parameters for the clothing tape compounds

To sum up, the following correlations of the Mooney relaxation parameters were observed:

- Linear correlation was observed between α and $M_{ret.30s}$ for both products, EPDM and NR (Fig. 5.13 and 5.15)
- The most significant Mooney relaxation parameters (Table 5.6) were all in good agreement for the automotive weather strip product
- However, in the case of the clothing tape compounds (Table 5.7), the values of *k* (similar in trend to MV) did not follow the trend observed with the rate of relaxation and $M_{ret.30s}$.

Main overall conclusions:

- De-vulcanised materials had a higher viscosity than the corresponding virgin material
- Closed-loop blends had a similar viscosity to the virgin compound
- Blends of clothing tape and automotive strip generally showed an increase in viscosity with a higher level of de-vulcanisate.
- Constant *k* showed a high linear correlation with Mooney Viscosity and is therefore, a characteristic of viscoelastic behaviour.
- Elasticity parameter, (α +1) is easier to interpret than α.
- Linear correlation exists between the Mooney relaxation parameters α and $M_{ret.30s}$ for both products, EPDM and NR
- $M_{ret.30s}$ can be potentially used instead of the rate of relaxation as a more reliable, easier to determine and understand characterisation parameter
- Hence, the Mooney relaxation test offers potential for being more accurate evaluation of the de-vulcanisation process than Mooney viscosity as it provides information on the

elastic component of unvulcanised material.

The curing characteristics of unvulcanised compounds can also be related to the efficiency of the de-vulcanisation process. The results of the curing characteristics and extrudability of the de-vulcanised and virgin materials and their blends have been considered in the next section of this chapter.

5.2 Processability and Curing characteristics

In addition to the Mooney Viscosity measurement, the quality and processability of unvulcanised rubber compounds were assessed by their extrudability and curing performance. Curing parameters (e.g. scorch time, optimum cure time, minimum torque, maximum torque, etc) are necessary for selecting the optimum processing conditions in order to achieve the desired properties in vulcanised rubber product. This section presents and analyses the results of the extrusion trials and curing test of the closed-loop tyre compounds. The results of the clothing tape and automotive weather strip compounds have been included for comparison purposes.

5.2.1 Processability: Extrusion trials

The processability of the closed-loop tyre compounds were assessed using a Plasti-Corder Brabender extruder equipped with a Garvey type die as detailed in section 4.3: Processability and Curing characteristics (Chapter 4).

Closed-loop tyre compounds:

After being warmed up on a two-roll mill, the compounds were cut into thin strips and continuously fed into the extruder until stable processing parameters were obtained. A sample of extrudate, approximately 250 mm in length was then taken for rating.

Processability observations of the closed-loop tyre materials during milling and extrusion are presented in Table 5.8. Pure de-vulcanisate proved to be difficult to process on its own (Fig.5.16) and therefore, only blends with virgin material were used for rating.

Table 5.8 Processing conditions for closed-loop tyre compounds

Sample Closed-loop tyre	Description	Die temperature, ºC	Screw speed, rpm	Torque, Nm/Kpm	Stock temperature at the die, ºC
1	Virgin rubber	120	50	18-22	111
2	5% blend	120	50	20	104
3	10% blend	120	50	15	96
4	15% blend	120	50	20	107
5	20% blend	120	50	29	111
6	25% blend	120	50	23-31	112
7	30% blend	120	50	24-30	113

Table 5.9 Processing observations and main comments for closed-loop tyre compounds

Sample Closed-loop tyre	Description	Milling comments	Extrusion comments
1	Virgin rubber	Very sticky, tendency to adhere to the back roll. The most difficult to mill	Sticky, smooth surface
2	5% blend	Sticky, tendency to adhere to the back roll	Sticky, smooth surface
3	10% blend	Less sticky, tendency to adhere to the back roll	Less sticky. Smooth curled extrudate
4	15% blend	Less sticky than samples 1-3, tendency to adhere to the back roll	Good quality extrudate
5	20% blend	More sticky than sample 4	Alternation of smooth and rough areas of the thick edge
6	25% blend	Easy to cut and mill	Occasional peeling on the thick part of the extrudate (approx.25 cm apart)
7	30% blend	Easiest to mill	Frequent peeling on the thick part of the extrudate (approx.every 3-5 cm)

It can be seen from the comments in Table 5.9 that the virgin compound (sample1) appeared to be sticky during milling and extrusion and that addition of the de-vulcanised material gradually improved the processability, with the optimum processing qualities achieved in sample 4 (15% blend). However, a further increase in de-vulcanised material (samples 5, 6 and 7) worsened the appearance of the extrudates.

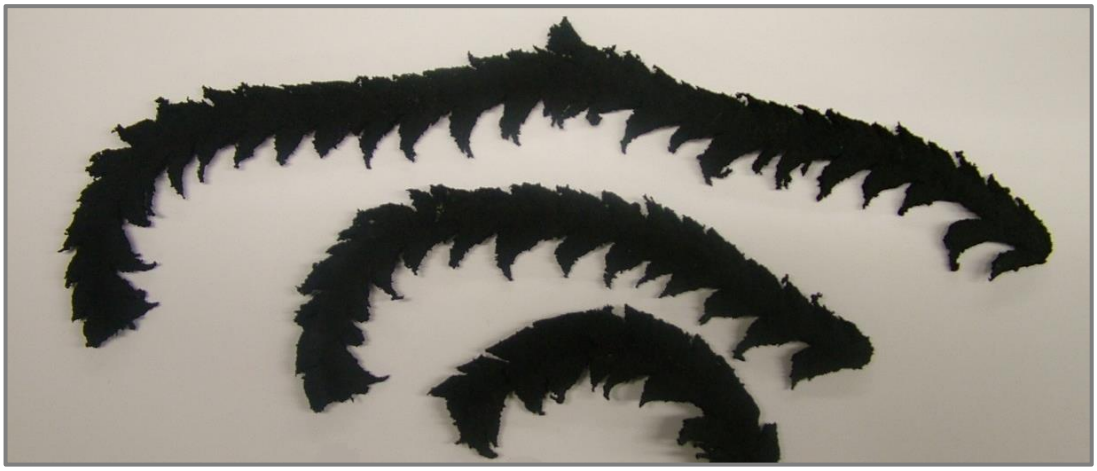


Fig. 5.16 Extruded samples of DeVulCO"2 closed-loop tyre material

Extruded closed-loop tyre samples (Fig. 5.17) were rated in accordance with the ASTM: D2230 standard[147] as explained in section 4.3: Processability and Curing characteristics (Chapter 4). The results of the rating are included in Table 5.10.

Table 5.10 Extrudability rating of unvulcanised closed-loop tyre compounds

Sample Closed-loop tyre	Description	Sharpness and continuity of the edge, (1-10)	Surface Rating, (A-E)
1	Virgin rubber	10	A
2	5% blend	8	A
3	10% blend	7	A
4	15% blend	8/9	A
5	20% blend	6/7	A
6	25% blend	5	B
7	30% blend	2	B

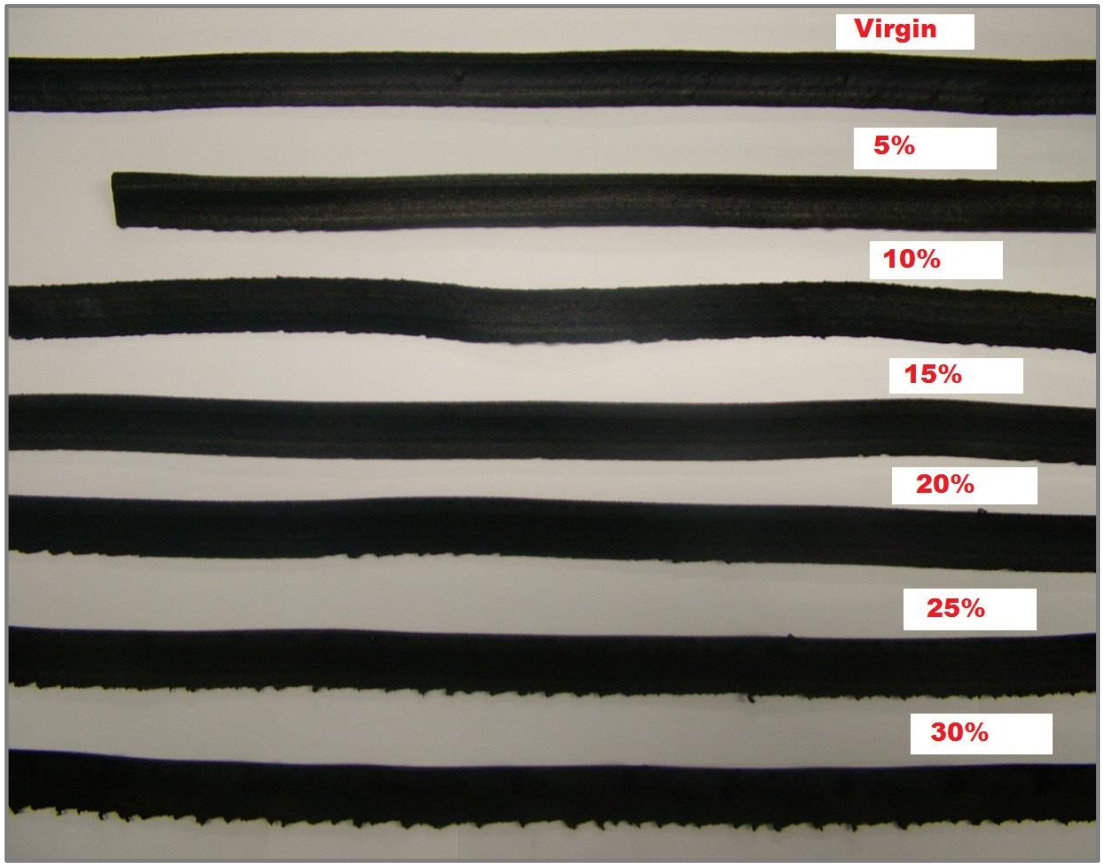


Fig. 5.17 Extruded samples (1-7) of closed-loop tyre blends and virgin material

As evident from Table 5.10 the best quality extrudate was obtained with the virgin compound (sample 1). Addition of the de-vulcanised material slightly impacted the sharpness and continuity of the edge. This became more prominent with sample 5 (20%). Both, surface and sharpness decreased in rating for samples 6 and 7.

To sum up, the following conclusions were drawn from the processing trial of the closed-loop tyre compounds:

- De-vulcanisate required blending with virgin compound in order to be processable
- Gradual increases in de-vulcanised material improved milling and extrusion, with the optimum performance at 15% addition
- Up to 20% of de-vulcanised material can be added to virgin material to retain an acceptable processing quality of extrudates
- Addition rates above 20% seemed to lead to a gradual decrease in surface quality and profile sharpness of extrudates

Clothing tape NR-based compounds:

The results of the extrusion trial for clothing tape compounds are presented in Tables 5.11 to 5.13.

Table 5.11 Processing conditions for clothing tape NR-based compounds

Sample NR	Description	Die temperature, ºC	Screw speed, rpm	Torque, Nm/Kpm	Stock temperature at the die, ºC
1	Virgin rubber	120	50	15	112
2	15% blend	120	50	15	113
3	25% blend	120	50	12	115

Table 5.12 Processing observations and main comments for clothing tape NR-based compounds

Sample NR	Description	Milling comments	Extrusion comments
1	Virgin rubber	Sticky and difficult to cross cut	Rough surface, low sharpness and continuity of the edge
2	15% blend	Sticky and difficult to cross cut	Combination of smooth and rough surfaces, improved sharpness and continuity of the edge
3	25% blend	Less sticky but difficult to cross cut	Rough surface, improved sharpness and continuity of the edge

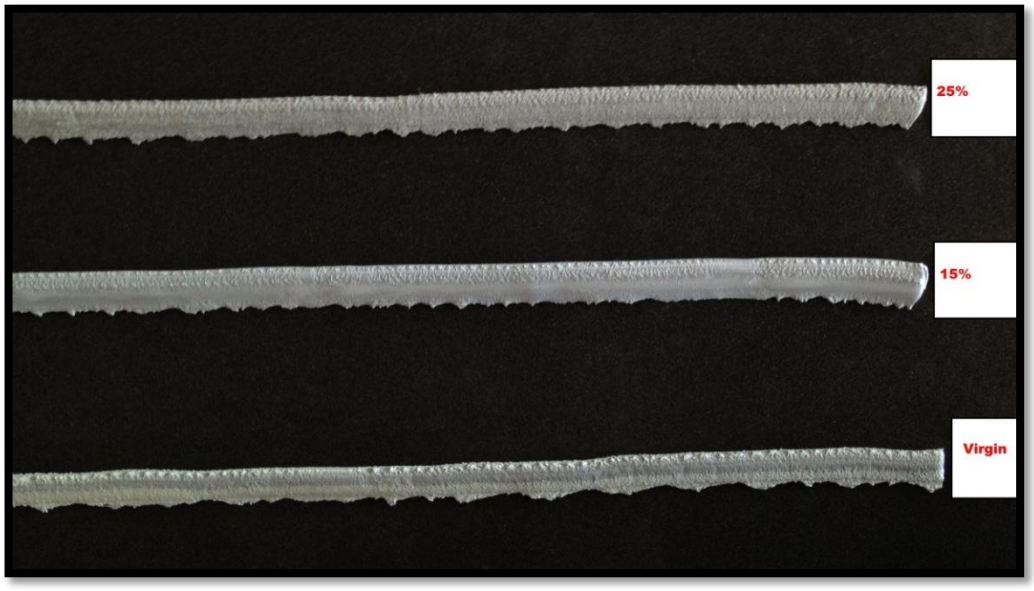


Fig. 5.18 Extruded samples (1-3) of clothing tape NR-based compounds

Table 5.13 Extrudability rating of unvulcanised clothing tape NR-based compounds

Sample NR	Description	Sharpness and continuity of the edge, (1-10)	Surface Rating, (A-E)
1	Virgin rubber	4	C/B
2	15% blend	6	B
3	25% blend	5	C/B

Overall, the following conclusions were drawn from the extrusion trial of the clothing tape compounds:

- Virgin compound was the most difficult to process and had the lowest extrudate rating
- Addition of de-vulcanised material reduced stickiness during milling and improved extrudability, with the optimum performance at 15% addition
- Addition rate above 20% (sample 3) seem to decrease the surface quality and profile sharpness of the extrudate

Automotive weather strip EPDM-based compounds:

The results of the extrusion trial for automotive weather strip compounds are presented in Tables 5.14 to 5.16.

Table 5.14 Processing conditions for automotive strip EPDM-based compounds

Sample EPDM	Description	Die temperature, °C	Screw speed, rpm	Torque, Nm/Kpm	Stock temperature at the die, °C
1	Virgin rubber	110	50	16	98
2	15% blend	110	38	13	97
3	25% blend	110	50	14	99
4	35% blend	110	50	16	100

Table 5.15 Processing observations and main comments for automotive strip EPDM-based compounds

Sample EPDM	Description	Milling comments	Extrusion comments
1	Virgin rubber	Sticky, tendency to adhere to the back roll	Medium quality sharpness and continuity of the edge, combined smooth and rough surfaces
2	15% blend	Sticky, tendency to adhere to the back roll	Medium quality sharpness and continuity of the edge, curly extrudate with combined smooth and rough surfaces
3	25% blend	Less sticky, tendency to adhere to the back roll	Very good sharpness and continuity of the edge, smooth surface
4	35% blend	Less sticky to compare to the samples 1-3, tendency to adhere to the back roll	Excellent sharpness and continuity of the edge, smooth surface

Fig. 5.19 Extruded samples (1-4) of automotive strip EPDM-based compounds

Table 5.16 Extrudability rating of unvulcanised automotive strip EPDM-based compounds

Sample EPDM	Description	Sharpness and continuity of the edge, (1-10)	Surface Rating, (A-E)
1	Virgin rubber	5	A/B
2	15% blend	5	A/B
3	25% blend	9	A
4	35% blend	8	A

Overall, the following conclusions were drawn from the extrusion trial of the automotive weather strip compounds:

- Gradual increase in de-vulcanised material improved milling and extrusion, with the optimum performance at 25% addition
- Good quality extrudate was still obtained at 35% addition

Die swell measurement

On exiting the die, an increase in cross sectional area (CSA) of the extrudate is expected due to a die swell effect. In general, the addition of ground tyre waste leads to improved processing and reduced die swell.[171] Hence, die swell measurement can be used to indicate the efficiency of de-vulcanisation.

However, evaluation of the die swell for the materials used in this study proved to be complex as their CSA appeared to be less than that of the die. This was particularly evident in the case of the virgin materials that were in general more sticky and difficult to extrude through the complex geometry die as compared to the blends. It has also been observed that the addition of de-vulcanised material in general improved processability and reduced the difference in the CSA of the extrudate and the die.

Apart from the processing difficulties, some reduction in the CSA of the extrudates could be explained by draw-down effect during extrusion, as the extruder didn't have a haul-off unit and the extrudate had to be advanced by hand on exiting the die. Use of a haul-off unit and a die with a less complex geometry could have offered more reliable measurements.

5.2.2 Curing Characteristics

The vulcanisation process leads to formation of the 3D network structure with a distinct number and types of cross-links, defining the most important properties of the resulting vulcanisate. The significance of vulcanisation on the structure and properties of vulcanised rubber products has been explained in Chapter 3 (Overview of techniques to characterise rubber network) of this thesis. As highlighted in section 2.5.3: Mechano-chemical de-vulcanisation (Chapter 2), the main drawbacks of de-vulcanised and re-vulcanised rubber compounds are the reduced scorch time and decreased or increased cure time. Changes in these parameters can lead to reduced processing safety and longer production times and have to be carefully monitored for high performance products (e.g tyres). At the same time, changes in curing characteristics can be used as a crude indication of the efficiency of the de-vulcanisation process. For example, the minimum torque (M_L) has been previously used by researchers[43] to compare the de-vulcanisation efficiency of various de-vulcanisation systems in compounds based on waste tyre rubber.

Therefore, the results of curing parameters of de-vulcanised rubber material, virgin compound and their blends have been compared in this study to determine their ability to indicate the efficiency of the de-vulcanisation process.

The curing characteristics of the rubber materials were determined by the oscillating disc Monsanto rheometer 100 as detailed in section 4.3: Processability and Curing characteristics (Chapter 4). The results of the analysed rheometer traces have been presented in Tables 5.17 to 5.19 with all parameters having the same meaning as defined in section 4.3. The conditions under which vulcanisation traces (rheographs) were obtained on the rheometer were: temperature 150±3°C, arc 3°; torque 0-100 dN m; timescale 60 min (30 min. for the clothing tape NR-based compounds).

Closed-loop tyre compounds:

Selected rheographs of the closed-loop tyre compounds are presented in Fig. 5.20 to Fig.5.23.

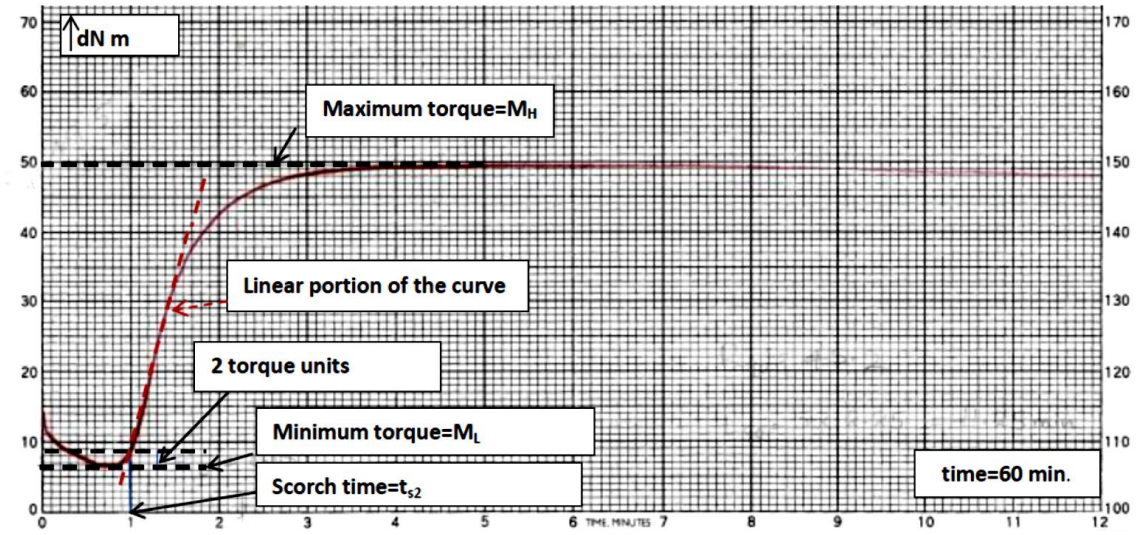


Fig. 5.20 Cure profile of the Virgin closed-loop tyre compound (sample 1, Table 5.17)

Fig. 5.20 Explains the determination of the main curing parameters by showing the position of the minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}) and the near linear portion of the curve from which the maximum cure rate (the slope of the line) was calculated. The scorch time was determined as the time related to the torque, 2 torque units above the minimum torque.

The plot of torque against time indicates processing (a scorch delay or induction region of the curve), curing (cure reaction region) and physical properties (postcure region) of a rubber compound.[174] With the start of curing, the rheometric torque starts to increase, yielding the slope that varies from one rubber compound to another. Ideally, after some time the torque attains its maximum value and plateaus out. However, in some cases, the torque starts to decrease (reverting curve) or carry on increasing with time (rising or marching curve). All three of these types of vulcanisation behaviour have been observed in the case of closed-loop compounds.

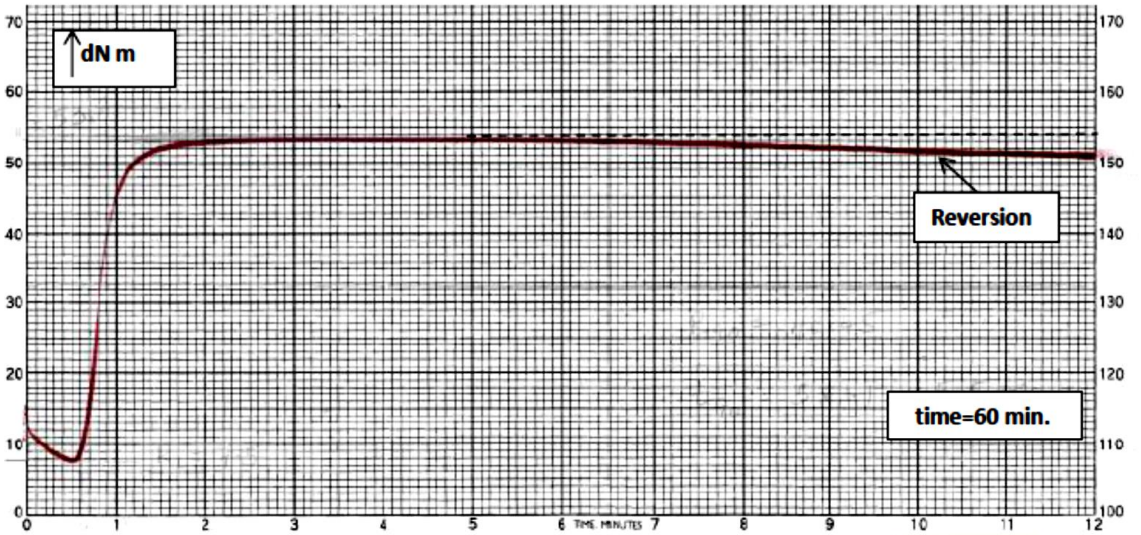


Fig. 5.21 Cure profile of the 10% blend closed-loop tyre compound (sample 3, Table 5.17)

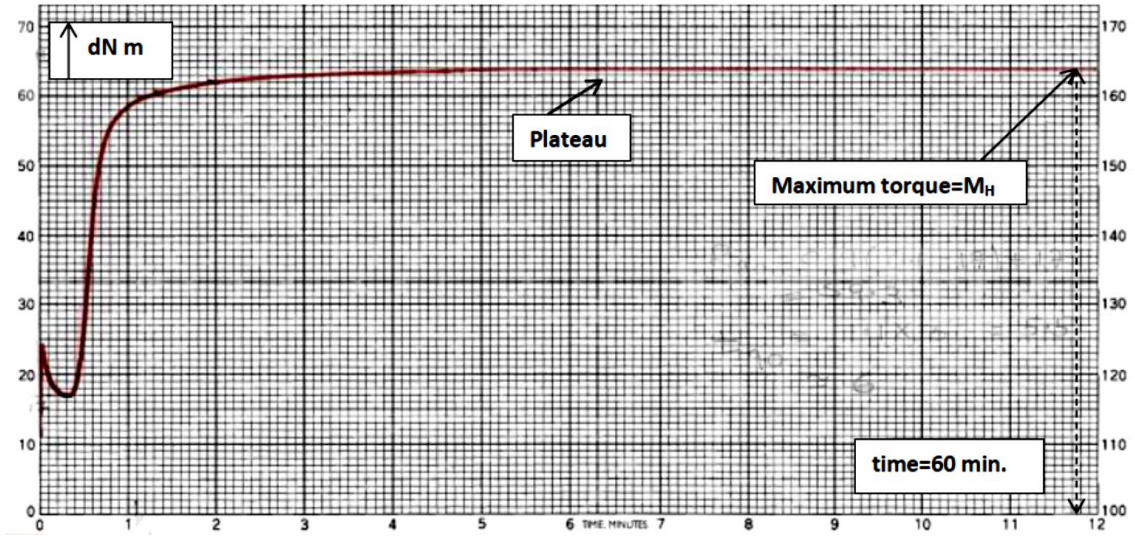


Fig. 5.22 Cure profile of the 30% blend closed-loop tyre compound (sample 7, Table 5.17)

It can be clearly seen from the Fig. 5. 20 to Fig. 5.22 and Table 5.17 that both, maximum and minimum torque increased with the addition of de-vulcanised material. On the other hand, the scorch time gradually decreased with increase in loading of DeVulCO"2. It has been also observed from the rheographs, that the addition of small amounts of de-vulcanised compound increased the tendency of the material to reversion (sample 2 and 3, Table 5.17), while the higher loading (sample 5, 6 and 7, Table 5.17) led to a plateau type of curve. However, pure de-vulcanisate (sample 8, Table 5.17) displayed a typical marching behaviour (Fig. 23) and its maximum torque was defined as the torque at 60 minutes.

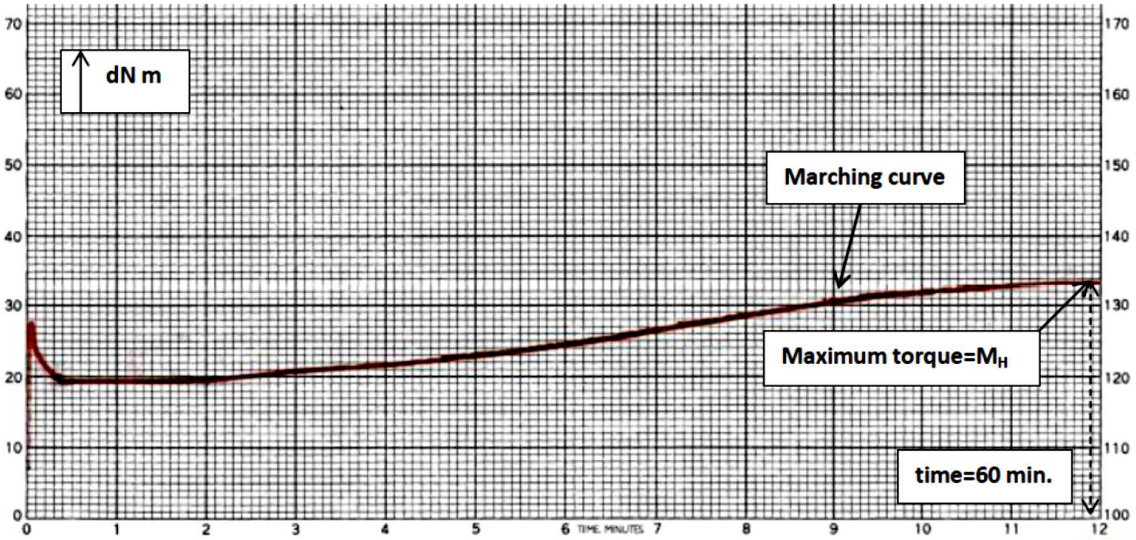


Fig. 23 DeVulCO"2 closed-loop tyre compound (sample 8, Table 5.17)

Table 5.17 Results of the curing test for closed-loop tyre compounds

Sample Closed-loop tyre	Description	M_L, dN m	M_H, dN m	M_H-M_L, dN m	Scorch time, t_{s2}, min	M_{90}, dN m	t_{90}, min	Cure rate index, min^{-1}	Max. cure rate, dN m min^{-1}
1	Virgin rubber	6.50	49.5	43.0	5.00	45.2	11.3	16.00	10.0
2	5% blend	7.00	54.0	47.0	4.00	49.3	7.50	28.6	16.3
3	10% blend	7.50	53.5	46.0	3.00	48.9	5.50	40.0	22.0
4	15% blend	10.0	56.5	46.5	2.63	51.9	5.00	42.2	23.6
5	20% blend	12.5	58.5	46.0	2.38	53.9	4.75	42.2	26.6
6	25% blend	14.5	61.5	47.0	2.25	56.8	5.00	36.4	27.3
7	30% blend	16.0	64.5	48.5	2.00	59.7	6.50	22.2	28.0
8	DeVul CO"2 rubber crumb	19.0	33.0	14.0	18.0	31.6	50.0	3.13	0.25

Fig. 5.24 is based on the change in the minimum torque and torque rise of the closed-loop blends. As the minimum torque is the measure of stiffness and viscosity of unvulcanised rubber compounds, the Mooney viscosity results were also included for comparison.

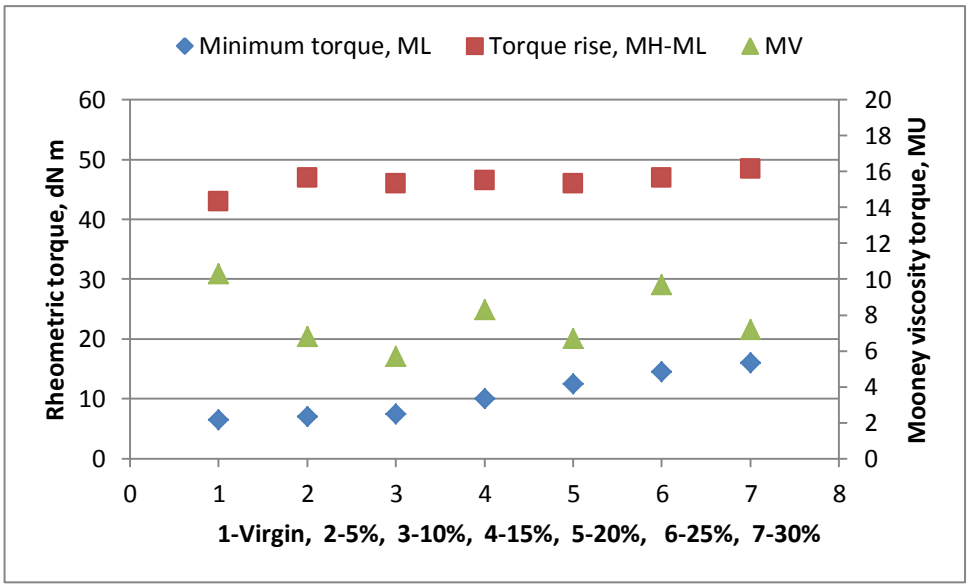


Fig. 5.24 Influence of de-vulcanisate loading on minimum torque and torque rise for closed-loop tyre compounds

As observed in Fig. 5.24, the minimum torque increased on addition of de-vulcanised material and continued to increase with increased loading of DeVulCO"2. As the minimum torque is related to the stiffness of the un-vulcanised rubber, increased values of the torque, M_L may indicate additional elastic contributions from the cross-links still remaining in the original rubber network[49]. These results are in good agreement with the general trend reported by Ramarad et al[175] when ground rubber tyre (GRT) crumb or de-vulcanised rubber tyre crumb (DRT) was blended with virgin compound. As reported by these researchers, the addition of GRT or DRT results in an increased minimum torque of the blend and generally increases with a higher loading of crumb. However, the increase in the torque tends to be lower with the addition of DRT than GRT due to the partial de-vulcanisation of the crumb and hence, its better flow in the matrix.

An increase in Mooney viscosity would be expected with an increase in M_L[175] but in the case of the closed-loop tyre compounds there was no clear correlation observed between the Mooney viscosity results and the minimum torque. The lack of correlation between these two parameters could possibly be due to the values of the minimum torque being overestimated. It is recognised[75] that the cold rotor in an oscillating disk rheometer (ODR) is the key drawback as compared to a moving disk rheometers (MDR), as the cold rotor prevents the rubber sample from reaching the required temperature as quickly. This is supported by evidence from a comparison of the rheographs for the virgin closed-loop tyre compound (Fig. 5.20) and blends (Fig. 5.21 and Fig. 5.22), showing insufficient time to reach the test temperature of 150ºC with the addition of DeVulCO"2, particularly

at higher loadings where the time reduces by half. Overestimation of the minimum torque is further supported by the relatively high value of the minimum torque for sample 7 (30% blend) compared to sample 8 (100% de-vulcanisate) in Table 5.17. This suggests that an increase in the minimum torque together with an increase in de-vulcanisate content is related to the decrease in scorch delay time, with vulcanisation starting before the rubber is fully up to the required temperature.

As noted earlier, the torque rise corresponds to the amount of cross-links introduced and hence, can be related to the efficiency of the de-vulcanisation process. As illustrated in Fig. 5.24, the torque rise increased by approximately 7% with a small addition of the de-vulcanised material but did not change significantly until sample 7 with a higher loading of the DeVulCO"2 (30% blend. This behaviour indicates that the addition of de-vulcanised material prompted formation of new cross-links. This can be further established through comparison with untreated ground rubber. It has been reported by Ishiaku et al[51] that introduction of untreated ground rubber in natural rubber vulcanisates tends to decrease torque rise, which decreases further with increased content of ground rubber. Ishiaku and co-workers explained this by the migration of sulphur from the rubber matrix into ground rubber, leading to a reduced availability of sulphur during the vulcanisation process and hence, reduced cross-link densities of ground rubber filled vulcanisates. It has to be noted, that the cold rotor in the ODR equipment is also likely to affect torque rise, which could be underestimated as a result and may therefore explain the plateau in torque rise observed in the middle range of DeVulCO"2 contents. As the de-vulcanised material is already cross-linked to some extent, the maximum torque, M_H can provide a more relevant measure of the total cross-linking. It is clear from Table 5.17 that M_H for the closed-loop tyre blends increases continuously with increasing DeVulCO"2 content, indicating an increase in the total level of cross-linking. Another explanation of the plateau in the torque rise comes from consideration of the nature of the blends that consist of two phases: virgin material and DeVulCO"2. Virgin material ("typical" truck tyre formulation, Appendix 1) is expected to contain active curatives, whereas the cure potential of the DeVulCO"2 only arises from the pendent groups formed during the de-vulcanisation process and some residual accelerators from the de-vulcanisation process. Hence, the diffusion of curatives from the virgin compound will reduce the level of cross-linking that may be achieved in that phase whilst increasing the level of cross-linking that may be achieved in the_DeVulCO"2 phase of the blend.

Fig. 5.25 below illustrates the change in the maximum cure rate and scorch time of closed-loop tyre compounds. It can clearly be seen that inclusion of de-vulcanised material in the blends leads to a decrease in scorch time which seems to be inversely proportional to the maximum cure rate.

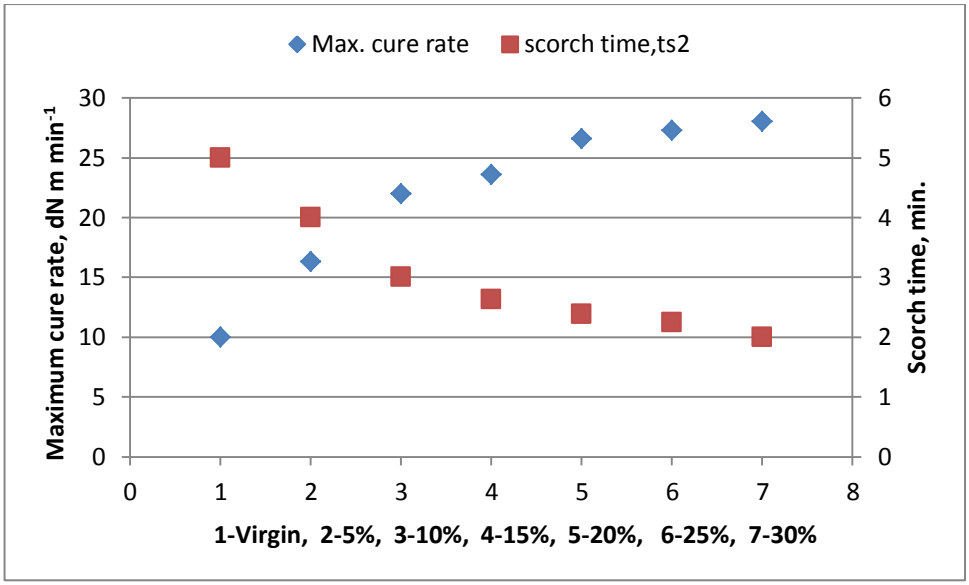


Fig. 5.25 Influence of de-vulcanisate loading on maximum cure rate and scorch time for closed-loop tyre compounds

Scorch time is an important curing characteristic as it indicates the start of the cross-linking process. Sufficient scorch time is required to ensure processing safety during the tyre production process. A literature review, carried out by Ramarad et al[175] outlined the reduction in scorch time of blends of virgin material and GRT (ground rubber tyre) or DRT (de-vulcanised rubber tyre) crumb. This reduction was attributed to the presence of unreacted chemicals or cross-link precursors in the GRT/DRT crumb or the presence of active cross-linking sites which accelerate the cross-linking reaction on heating. In addition, in the case of DRT crumb scorch times for the blends appeared to be much shorter than for the pure de-vulcanisate[43]. The same reason for a reduction in scorch time of the blends was mentioned by Phadke at al[176] in their studies on de-vulcanised rubber and blends with virgin material obtained through the mechano-chemical de-vulcanisation process.

As evident from Fig. 5.25, the scorch time reduced by 20% with addition of 5% DeVulCO"2 (samples 2, Table 5.17) and continued to decrease with further loading of de-vulcanised material. However, the decrease in scorch time became less prominent above the 15% loading (samples 4 to 7, Table 5.17). The decrease in scorch time of the blends can be explained by the migration of the vulcanisation additives from the virgin compound to DeVulCO"2 as well as the migration of the active species from the DeVulCO"2 to virgin material. As explained in Chapter 3, vulcanisation accelerators are carefully selected to allow sufficient scorch time. Accordingly, a virgin compound would be based on the delayed action accelerators (Table 3.1, Chapter 3) whereas the active chemicals in the de-vulcanised material seem to be semi-fast to fast type of accelerators (Fig. 3.3 and Fig. 3.4, Chapter 3) that would be expected to increase the maximum cure rate and to reduce the scorch time. In contrast, the scorch time of the pure de-vulcanisate (sample 8, Table 5.17) increased from 5 to 18 minutes while the maximum cure rate significantly decreased. As explained

in Chapter 2, DeVulCO"2 is a patented[55] de-vulcanisation technology with a similar de-vulcanisation chemistry to De-Link technology[46,52]. The interaction of a chemical treatment, mechanical shear and heat facilitates selective cross-link breaking and formation of rubber bound pendent groups ready for re-vulcanisation, in a way similar to the Sekhar-Kormer-Sotnikova reaction[47] (Fig. 2.7, Chapter 2). Hence, the curing potential of 100% de-vulcanised material comes from the pendent groups created in the de-vulcanisation process, not all of which may be capable of re-forming cross-links. This explains the significant decrease in the maximum cure rate and increase in the scorch time for sample 8 (Table. 5.17).

On the other hand, the maximum cure rates of the blends increased with addition of de-vulcanised material. However, this increase became less prominent above the loading of 15% (samples 4 to 7, Table 5.17). This can be explained in the same way as for the decrease in scorch delay time in the blends. The maximum cure rate is a good indication of new cross-link formation as it occurs before the cross-links shorten as the network starts to mature, as illustrated in Fig. 3.7 (Chapter 3).

The cure rate index provides an indication of how long the compound will require to be vulcanised and therefore is a practical measure of speed of cure. It can be seen from Fig. 5.26 that the inclusion of de-vulcanised material leads to an increase in the average speed of cure with the peak between 15% and 20% of DeVulCO"2. Any further addition of de-vulcanised material (sample 6 and 7, Table 5.17) leads to a reduction in the cure rate.

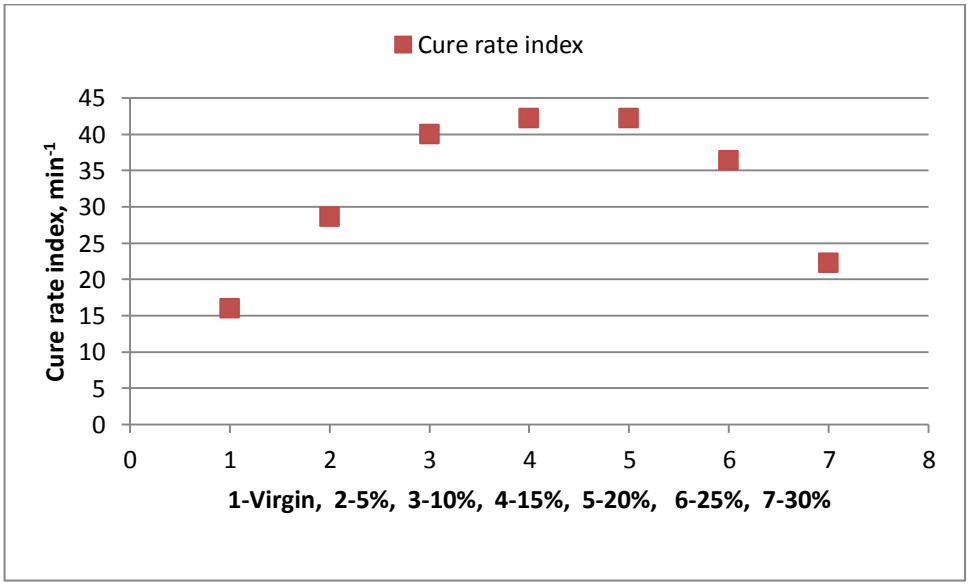


Fig 5.26 Influence of de-vulcanisate loading on minimum torque and cure rate index for closed-loop tyre compounds

The results presented in Fig. 5.26 show the complex effect of the DeVulCO"2 on the cure rate index and could be related to the rates of two competing reactions: the formation of new cross-links and the loss of cross-links during vulcanisation through inefficient cross-link shortening

reactions. When the process of the loss of cross-links overtakes the formation of new cross-links, the reversion is observed (Fig. 5.21). As explained in Chapter 3, reversion leads to chemical changes and impacts the properties of the vulcanisate.

The process of losing cross-links, as the network structure matures during vulcanisation, begins before the maximum torque is reached and therefore, any chemistry that affects the rate of loss of cross-linking by making the cross-link shortening process more efficient, will affect the approach to maximum torque as observed in Fig. 5.22. For example, a similarly slow approach to maximum torque as in Fig. 5.22 is observed when high levels of fatty acids (e.g. stearic acid) are added to improve the performance of truck tyre treads[177]. This effect is caused by the high fatty acid level increasing the recycling of the zinc-accelerator complex, which also contains fatty acid, thereby improving the efficiency of the cross-link shortening process. Although a similar mechanism may be operating in the case of the closed-loop tyre material, the exact explanation of the observed behaviour cannot be established due to a lack of information on the vulcanisation/de-vulcanisation chemicals used.

The observed peak in the cure rate index (Fig. 5.26) as a function of the DeVulCO”2 content may be related to the balance between the rate of cross-link insertion that seems to be increased by the presence of the de-vulcanisate and the rate of cross-link loss that appears to be decreased by the presence of the de-vulcanisate. Low levels of DeVulCO”2, increase the rate of cross-link formation but do not prevent the loss of cross-links due to the cross-link shortening reactions, leading to reversion (Fig. 5.21). However, higher levels of the de-vulcanisate reduce the inefficiency of the cross-link shortening reactions, leading to observed plateau (Fig. 5.22).

Clothing tape NR-based compounds:

Table 5.18 Results of the curing test for clothing tape NR-based compounds

Sample NR	**Description**	**M_L, dN m**	**M_H, dN m**	**M_H-M_L, dN m**	**Scorch time, t_{s2}, min**	**M_{90}, dN m**	**t_{90}, min**	**Cure rate index, min^{-1}**	**Max. cure rate, dN m min^{-1}**
1	Virgin rubber	20.0	60.0	40.0	6.25	56.0	12.00	17.4	8.00
2	15% blend	19.0	63.0	44.0	3.25	58.6	5.50	44.4	26.0
3	25% blend	22.0	66.0	44.0	2.75	61.6	5.75	33.3	27.0

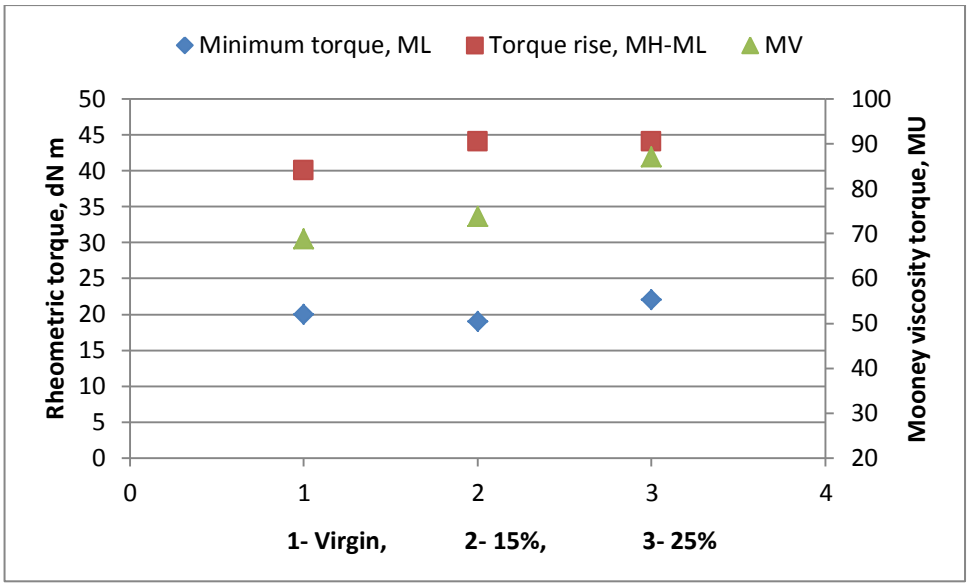


Fig. 5.27 Influence of de-vulcanisate loading on minimum torque and torque rise for NR-based compounds

It can be seen from Fig. 5.27 that the minimum torque, slightly reduced with addition of de-vulcanised material (sample 2, Table 5.18) and then increased by approximately 14% with further addition of DeVulCO"2 (sample 3, Table 5.18). However, the torque rise, increased with addition of DeVulCO"2 (sample 2, Table 5.18) but did not change with a higher loading in de-vulcanised material (sample 3, Table 5.18). This behaviour is similar to the one observed with the closed-loop tyre blends and hence, can be explained by the same reasoning.

Although, the minimum torque did not show any correlation with the Mooney viscosity values it did match the rate of relaxation (Fig. 5.28) and hence, the elasticity parameter and $M_{ret.30s}$. It could be related to the fact that the ODR is a small-strain dynamic measurement and hence, sensitive to elasticity. Therefore, the Mooney relaxation parameters appear to be more sensitive, and best suited for characterisation the de-vulcanisation process.

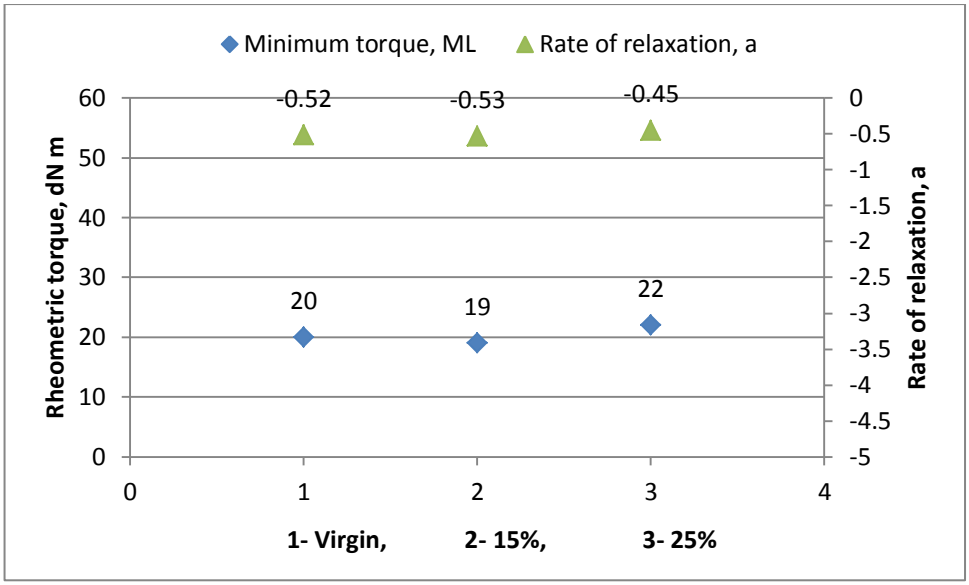


Fig. 5.28 Relationship between the minimum torque and the rate of relaxation for clothing tape NR-based compounds

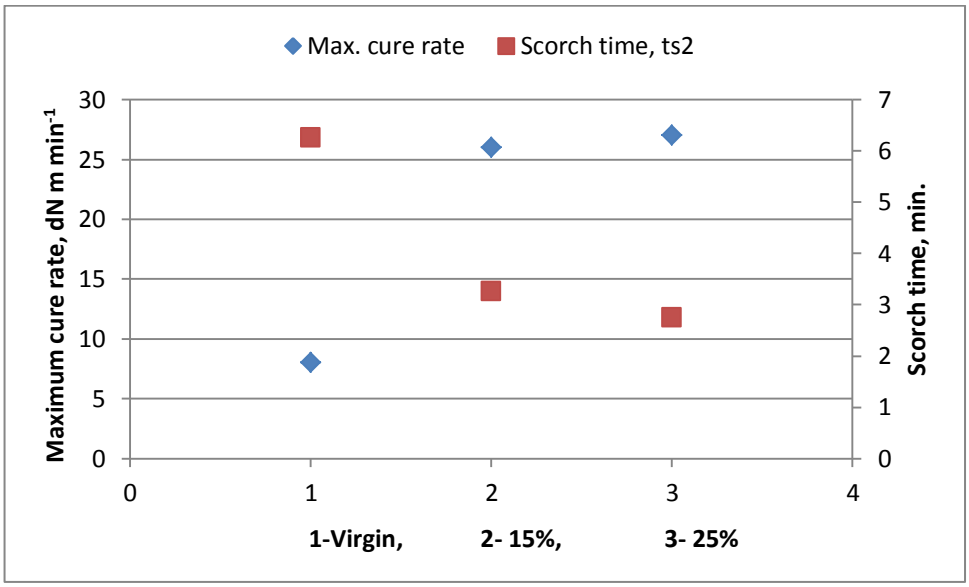


Fig. 5.29 Influence of de-vulcanisate loading on maximum cure rate and scorch time for NR-based compounds

As with the results of the closed-loop blends, the scorch time of the clothing tape material reduced by 48% with the addition of 5% DeVulCO"2 (samples 2, Table 5.18) and continued to decrease on further loading of de-vulcanised material (sample 3, Table 5.18). On the other hand, the maximum cure rates of the blends increased with the addition of de-vulcanised material (Fig. 5.29). The reasons for decrease in the scorch time and increase in the maximum cure rates of the blends are the same as for the closed-loop tyre compounds.

Selected rheographs of the clothing tape NR-based compounds are presented in Fig. 5.30 and Fig.

5.31. It is clear from the rheograms that the inclusion of de-vulcanised material reduces the induction period (scorch time), increases the slope of the near linear portion of the curve (maximum cure rate) and leads to an earlier plateau of the torque. However, it has to be noted that the clothing tape compounds are not closed – loop materials and hence, the virgin material can be quite different from the de-vulcanised material.

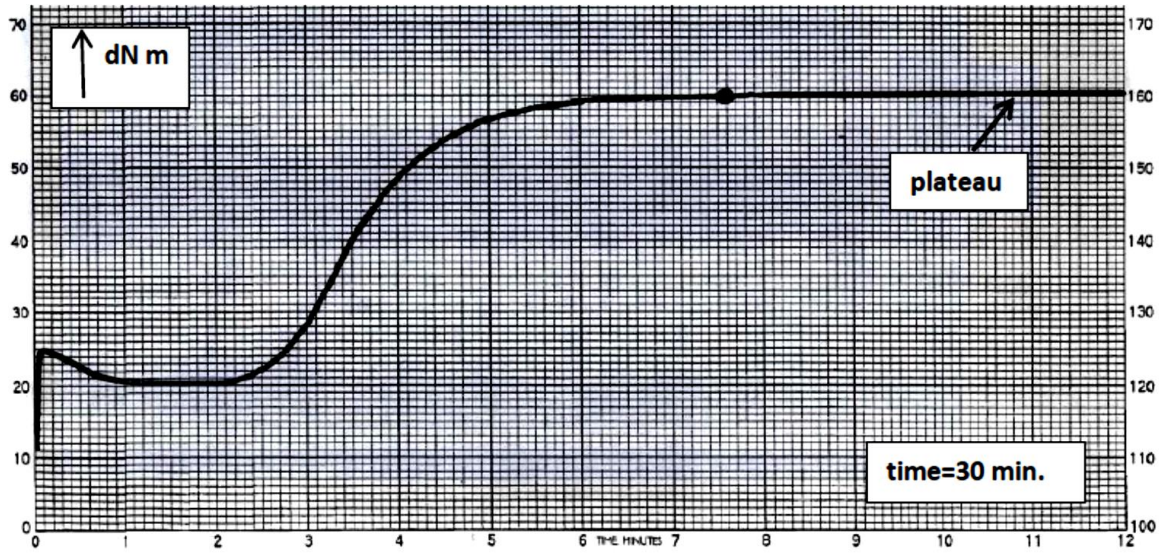


Fig. 5.30 Cure profile of the virgin clothing tape NR-based compound (sample 1, Table 5.18)

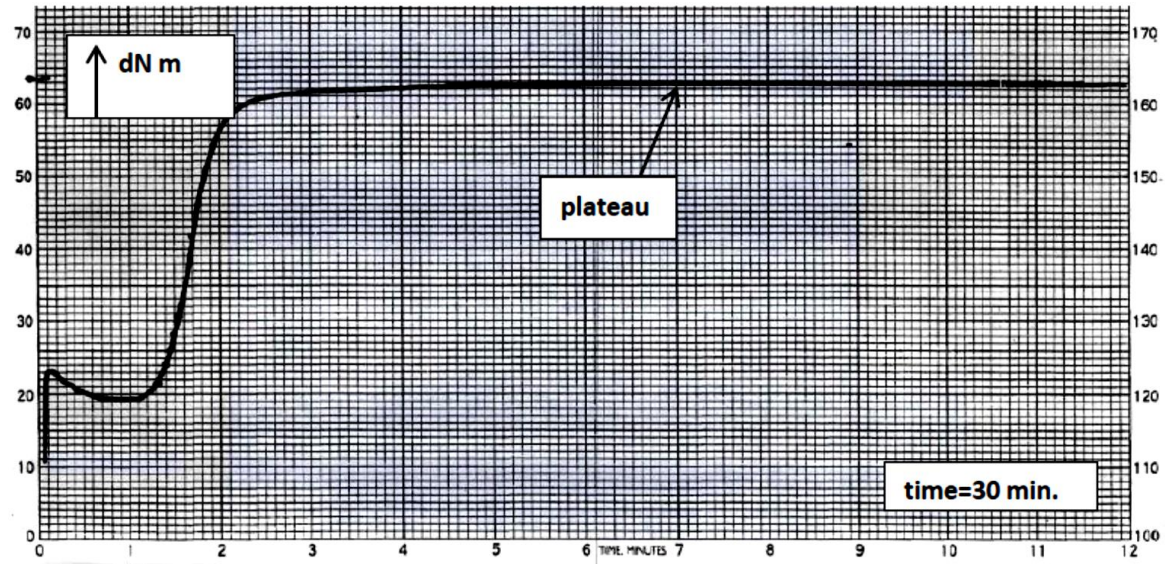


Fig. 5.31 Cure profile of the 15% blend clothing tape NR-based compound (sample 2, Table 5.18)

The cure rate index (Fig. 5.32) increased with the addition of de-vulcanised material (sample 2, Table 5.18) and reduced with further increase in loading of DeVulCO”2. The observed behaviour is similar to that displayed by the closed-loop tyre compounds (Fig.5.26), with the maximum value of the cure rate attained at 15% addition.

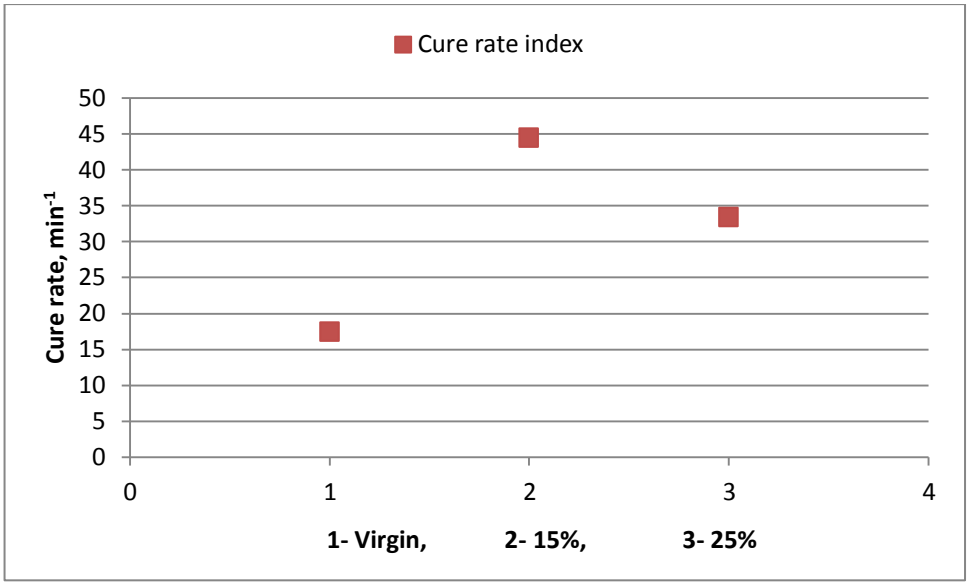


Fig. 5.32 Influence of de-vulcanisate loading on minimum torque and cure rate index for NR-based compounds

Automotive weather strip EPDM-based compounds:

Table 5.19 Results of the curing test for automotive strip EPDM-based compounds

Sample EPDM	Description	M_L, dN m	M_H, dN m	M_H-M_L, dN m	Scorch time, t_{s2}, min	M_{90}, dN m	t_{90}, min	Cure rate index, min^{-1}	Max. cure rate, dN m min^{-1}
1	Virgin rubber	13.0	58.0	45.0	3.50	53.5	29.0	4.00	3.45
2	15% blend	16.0	53.0	37.0	3.50	49.3	21.5	5.60	3.80
3	25% blend	18.0	50.0	32.0	4.00	46.8	14.0	10.0	3.50
4	35% blend	22.0	50.0	28.0	4.50	47.2	16.5	8.30	2.57

It can be seen from Fig. 5.33, that consistent with the results observed with the closed-loop tyre compounds , the minimum torque of the automotive strip compound increased initially by 23% (sample 2, Table 5.19) and continued to increase with further loading of DeVulCO"2 (samples 3 and 4, Table 5.19). As already mentioned, this could be as a result of the presence of remaining cross-links in the de-vulcanised material.

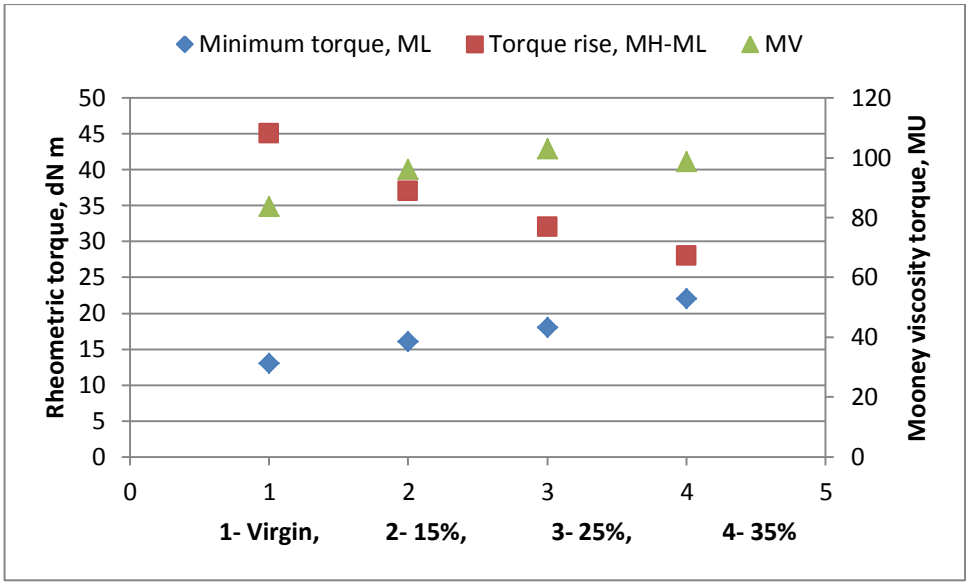


Fig. 5.33 Influence of de-vulcanisate loading on minimum torque and torque rise for EPDM-based compounds

In contrast to the two materials considered earlier, the torque rise for the automotive strip compound reduced with the addition of de-vulcanised material (sample 2, Table 5.19) and continued to decrease with further addition of DeVulCO"2 (samples 3 and 4, Table 5.19). The same trend was observed by Sabzekar et al[178] who used a twin-screw extruder and disulphide oil to de-vulcanise EPDM-based automotive strip waste. De-vulcanised rubber (20 wt% and 40 wt% respectively) was then blended with the virgin rubber and compounded with the rest of the additives used in a "typical" automotive strip formulation (Appendix 2). Reduction in the torque rise was also reported by Mohaved et al[179] when 20 wt% and 60 wt% of virgin EPDM rubber was replaced respectively by de-vulcanised material in the case of an automotive strip application. The de-vulcanisation process was carried out in an industrial autoclave and assisted by the use of MBTS (Dibenzothiazol-2-yl Disulphide) and TMTD (tetramethylthiuramdisulphide) accelerators and aromatic and aliphatic oils.

The values of the torque rise for EPDM blends (Table 5.19) revealed that the DeVulCO"2 appeared not to be curing as the torque rise was approximately proportional to the amount of virgin compound in the blend and could therefore account for 95% of the torque rise. The decrease in the torque rise was also accompanied by a decrease in the maximum torque, indicating that a lower number of cross-links were formed when de-vulcanised material was added. As mentioned in Chapter 3, EPDM rubber has low unsaturation and hence, requires a more complex acceleration system for vulcanisation. Inevitably, the cure potential of de-vulcanised EPDM rubber is relatively low. Therefore, the observed results are due to a combination of the low efficiency of de-vulcanisation and the low level of unsaturation, especially as a significant proportion of the unsaturation would have already been lost during the first vulcanisation.

As evident from the Fig. 5.33 no clear correlation exists between the minimum torque and the Mooney viscosity values. However, as illustrated in Fig. 5.34 some form of a relationship does exist between the minimum torque and the rate of relaxation (increase in values of M_L and α with increase in DeVulCO"2 loading). This can be attributed to a better sensitivity of the ODR equipment (small-strain dynamic measurement) to elasticity.

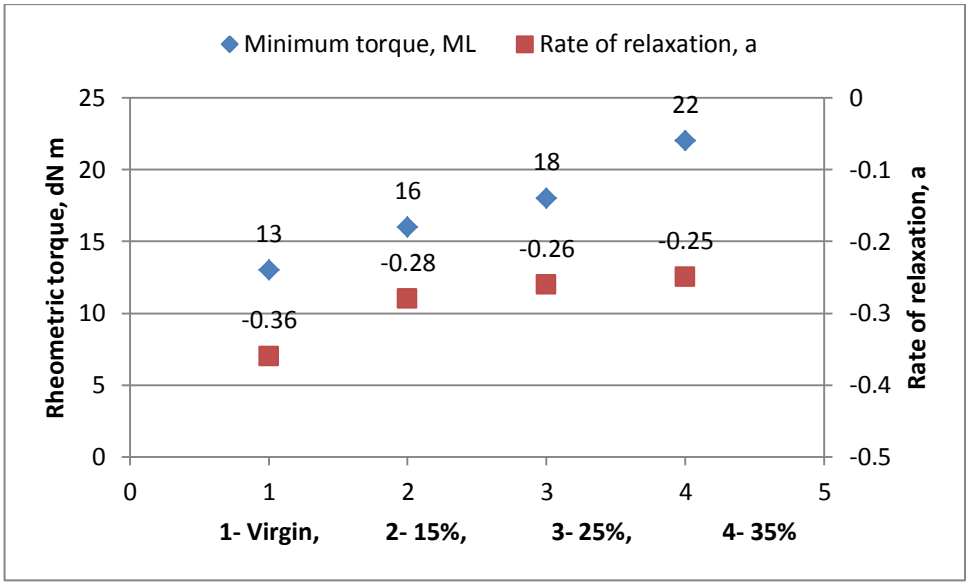


Fig. 5.34 Relationship between the minimum torque and the rate of relaxation for EPDM-based compounds

It can be seen in Fig. 5.35 that the scorch time was not affected by a 15% addition of DeVulCO"2 but increased steadily with further increase in de-vulcanised content (sample 3 and 4, Table 5.19). Mohaved et al[179] reported that scorch time in a similar study was not affected by the addition of de-vulcanised material (up to 60 wt%). On the other hand, M. Sabzekar observed a decrease in scorch time when 40 wt% of de-vulcanised material was used as a substitute for virgin rubber in a similar application.

The maximum cure rate showed an increase with the addition of 15% de-vulcanised material but continuously decreased with higher additions of DeVulCO"2 (samples 3 and 4, Table 5.19).

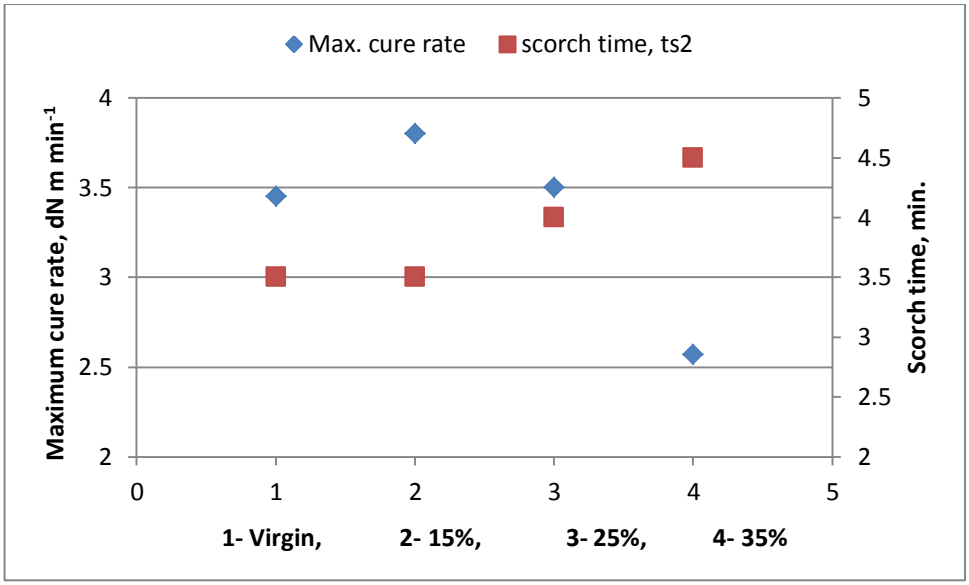


Fig. 5.35 Influence of de-vulcanisate loading on maximum cure rate and scorch time for EPDM-based compounds

The above results can be explained by the loss of curatives from the virgin compound to the relatively unreactive DeVulCO"2. It seems that with low quantities of de-vulcanised material, the active vulcanising species from the DeVulCO"2 exerts a greater effect than the migration of curatives from the virgin compound, but at higher levels the loss of curatives becomes the dominant effect, leading to an increased scorch time and reduced maximum cure rate.

Selected rheographs of the automotive strip EPDM-based compounds are presented in Fig. 5.36 and Fig. 5.37. It is clear from the rheograms that the inclusion of de-vulcanised material changed the marching behaviour of the torque to plateau. However, it has to be noted that as with NR-based clothing tape compounds, EPDM compounds are also not closed – loop materials and hence, virgin material can be quite different from the de-vulcanised material.

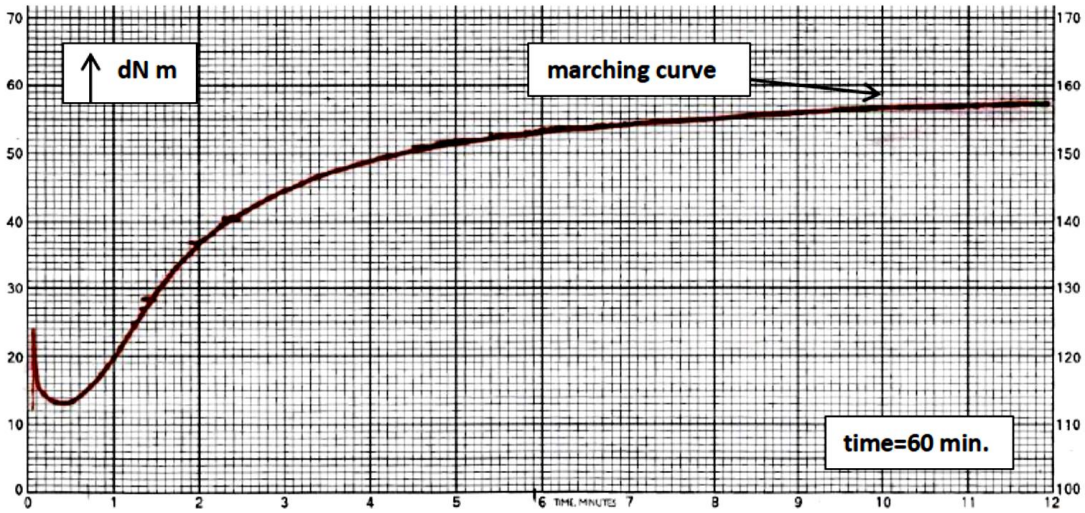


Fig. 5.36 Cure profile of the virgin automotive strip EPDM-based compound (sample 1, Table 5.19)

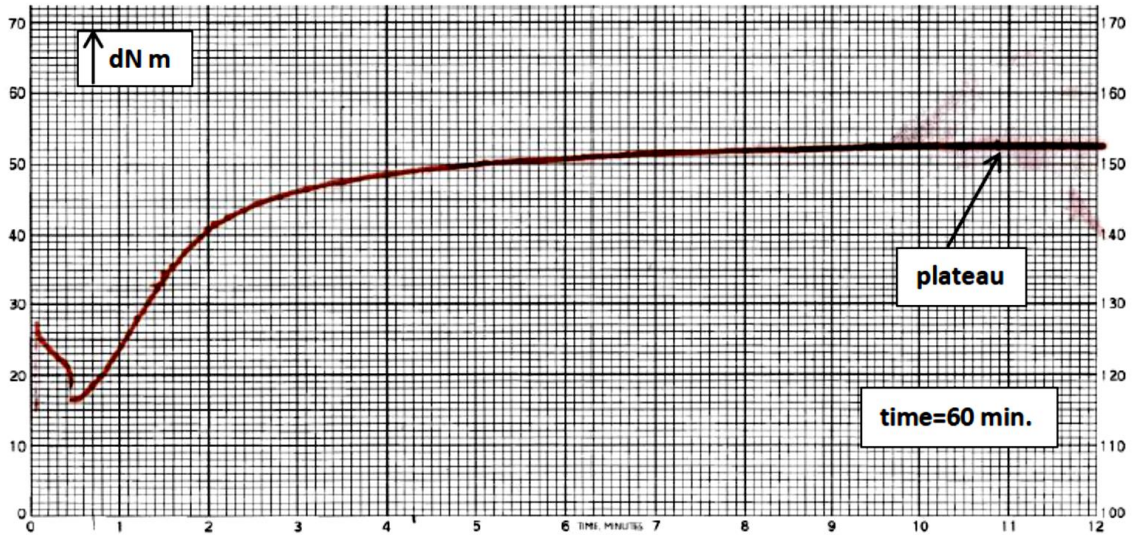


Fig. 5.37 Cure profile of the 15% blend automotive strip EPDM-based compound (sample 2, Table 5.19)

The cure rate index of EPDM-based compounds (Fig. 5.38) increased with the addition of de-vulcanised material (sample 2, Table 5.19) but reduced with further increase in loading of DeVulCO"2. The observed behaviour is similar to the closed-loop tyre compounds (Fig.5.26) and clothing tape NR-based compounds (Fig. 5.32). However, the maximum value of the cure rate index for EPDM-based compounds corresponds to the 25% loading and is slightly higher than in the case of the closed-loop tyre material (15% to 20% loading) and clothing tape compounds (15% loading). A difference in behaviour between the EPDM and NR based compounds can be explained by the difference in the cure system used. EPDM compounds have complex accelerator systems to compensate for the lower concentration of unsaturation of the rubber. The cure rate index was reported[178,179] to increase with the addition and progressive increase in the amount of de-vulcanised EPDM-based automotive waste material used to replace virgin rubber in an automotive strip application.

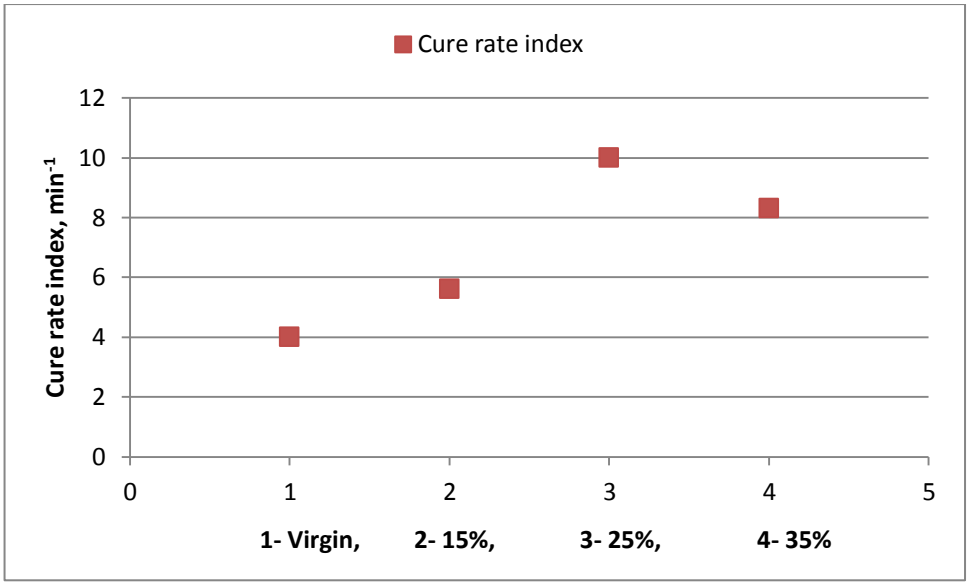


Fig. 5.38 Influence of de-vulcanisate loading on minimum torque and cure rate index for EPDM-based compounds

The summary of changes of the most significant curing parameters as a result of the addition of de-vulcanised material for all three products is outlined in Table 5.20

Table 5.20 Summary of the main curing parameters for closed-loop, clothing tape and automotive weather strip compounds

Sample	M_L, dN m	M_H-M_L, dN m	Scorch time, t_{s2}, min	Cure rate index, min^{-1}	Max. cure rate, dN m min^{-1}
Closed-loop tyre compounds:					
-Initial addition of DeVulCO"2	increase	increase	decrease	increase	increase
-Further addition	increase	stable	decrease	max. at 15% to 20% loading, then decrease	increase
-100% DeVulCO"2	increase	decrease	increase	decrease	decrease
NR-based clothing tape compounds:					
-Initial addition of DeVulCO"2	slight drop	increase	decrease	increase & max. at 15%	increase
-Further addition	increase	no change	decrease	decrease	increase
EPDM-based automotive strip compounds:					
-Initial addition of DeVulCO"2	Increase	decrease	no change	increase & max. at 25%	increase & max. at 15%
-Further addition	increase	decrease	increase	decrease	decrease

The following conclusions were drawn from the curing characteristics results:

Minimum torque, M_L

- Minimum torque relates to the stiffness and viscosity of unvulcanised rubber. In general, the minimum torque progressively increased with the addition of de-vulcanised material.
- The rate of relaxation showed a better sensitivity to the changes in minimum torque than Mooney viscosity and hence, may provide a better indication of de-vulcanisation efficiency.

Torque rise, M_H-M_L

- The torque rise relates to the formation of new cross-links. The torque rise, increased with the initial addition of de-vulcanised material for both, the closed-loop tyre blend and NR-based clothing tape blend. However, it did not changed significantly on further addition.
- The torque rise reduced in the case of the automotive weather strip compounds.
- In the next section, torque rise has been considered in the context of the swelling measurements (e.g volume fraction of swollen rubber) to establish whether it relates to the efficiency of the de-vulcanisation process.

Scorch time, t_{s2}

- Scorch time is an important processing safety parameter. Scorch time significantly increased for the 100% de-vulcanised closed-loop tyre compound. However, the scorch times of the blends were lower than for the virgin compound.
- Scorch time also decreased in the case of the clothing tape blends
- For both materials, increased loading of de-vulcanised material resulted in progressive decreases in the scorch time of the blends
- In practical applications, de-vulcanised material is going to be used in blends and hence, further adjustments to the de-vulcanisation/re-vulcanisation process may be required.
- On the upside, excellent results were observed in the case of the automotive weather strip blends. There was no reduction in the scorch time with 15% loading and higher loadings led to an increase in the scorch time.

Maximum cure rate

- The maximum cure rate increased following the initial addition of de-vulcanised material for all three materials.
- Increased loadings of De-VulCO”2 led to further increase in the maximum cure rate except

for EPDM blends, where a decrease in the maximum cure rate was observed at higher loadings (sample 3 and 4, Fig. 5.35).

- The maximum cure rate of 100% de-vulcanised closed-loop tyre compound was approximately 40 times lower than that for virgin material.

Cure rate index

- The cure rate index relates to the speed of vulcanisation. Similar to the trend observed with the maximum cure rate, the cure rate index increased with the initial addition of de-vulcanisate for all three materials. This could be beneficial to production efficiency.
- Increased loadings of De-VulCO"2 led to further increase in the cure rate index until a maximum value (between 15% and 25% loading, depending on the material) was achieved. Further increases in de-vulcanisate, led to a decrease in the cure rate index.
- However, the cure rate index of the pure closed-loop tyre de-vulcanisate was approximately 5 times less than the corresponding virgin compound, highlighting the need of blending for practical use.

5.3 Swelling measurements

The usefulness of swelling measurements to characterise the rubber network is detailed in section 3.3 (Swelling measurements) of Chapter 3. The Flory-Rehner equation (equation 5, Chapter 3) or modified Flory-Rehner equation (equation 6, Chapter 3) can be employed to determine the physically effective cross-link density of rubber by using the results of the swelling measurements. However, as explained in Chapter 3 (Swelling measurements) both equations are only valid for unfilled rubber compounds and hence, are not suitable for tyres. Additional complications in characterising ELT by using the cross-link density parameter arise from the fact that the tyre compound is a blend of rubbers with each rubber phase having a different cross-link density and a different polymer-solvent interaction parameter.

Therefore, the volume fraction of swollen rubber that is related to the physically effective cross-link density of rubber (equation 9, Chapter 3) was used in this study to characterise the rubber network. In order to overcome common errors, highlighted by Valentin et al[106] the amount of polymer and insoluble ingredients (eg. ZnO, fillers) were accurately determined by TGA. In addition, the density of rubber was calculated for each rubber sample using the procedure outlined in section 4.4 (Swelling measurements, Chapter 4). The density of toluene at 25^0C was taken[180] as 0.862 g cm^{-3}. The results of the swelling measurements have been presented and discussed in this section.

Closed-loop tyre compounds:

All rubber samples were first extracted with acetone to remove the non-rubber substances (activators, accelerators, etc) and swollen to equilibrium as detailed in section 4.4 (Swelling measurements) of Chapter 4. The weight of each sample in grams, before the acetone extraction (m_i) and when dry after the acetone extraction(m_e), were recorded. In addition, the weight of each sample at the equilibrium swelling in toluene (m_s) together with the deswollen dry weight (m_d) were also determined and used in equation 9 (Chapter 3) to calculate the amount of sol and the volume fraction of rubber in swollen vulcanisate. The results of the swelling measurements are presented in Table 5.21. Details of other relevant values (e.g. rubber density and amount of polymer) together with calculations of the sol portion and the volume fraction of rubber in swollen vulcanisate have been included in Appendix 3 (Tables 1 to 9).

Table 5.21 Results of the swelling measurements in toluene for closed-loop tyre compounds

Compound type (3 samples were used for each material)	**Initial weight of sample, m_i grams**	**Dry weight after acetone extraction, m_e, grams**	**Swollen to equilibrium in toluene weight, m_s grams**	**Deswollen (dried) weight, m_d grams**	**Volume fraction of swollen rubber, V_r**
Virgin 3 samples **Average** Stand. deviation	0.1616 0.1633 0.1597	0.1256 0.1269 0.1241	0.3876 0.3688 0.3600	0.1245 0.1266 0.1233	0.1927 0.2093 0.2083 **0.2034** ±0.0093
5% blend 3 samples **Average** Stand. deviation	0.1830 0.1709 0.1690	0.1436 0.1341 0.1326	0.4291 0.3952 0.3901	0.1428 0.1334 0.1314	0.2221 0.2258 0.2248 **0.2242** ±0.0019
10% blend 3 samples **Average** Stand. deviation	0.1570 0.1527 0.1526	0.1233 0.1199 0.1198	0.3568 0.3506 0.3481	0.1230 0.1197 0.1197	0.1915 0.1894 0.1911 **0.1907** ±0.0012
15% blend 3 samples **Average** Stand. deviation	0.1507 0.1512 0.1430	0.1184 0.1188 0.1123	0.3455 0.3315 0.3117	0.1188 0.1181 0.1118	0.2258 0.2345 0.2367 **0.2323** ±0.0058

Table 5.21 Results of the swelling measurements in toluene for closed-loop tyre compounds (cont.)

Compound type (3 samples were used for each material)	**Initial weight of sample, m_i grams**	**Dry weight after acetone extraction, m_e, grams**	**Swollen to equilibrium in toluene weight, m_s grams**	**Deswollen (dried) weight, m_d grams**	**Volume fraction of swollen rubber, V_r**
20% blend 3 samples **Average** Stand. deviation	0.1625 0.1557 0.1503	0.1275 0.1221 0.1179	0.3505 0.3405 0.3264	0.1267 0.1212 0.1174	0.2303 0.2260 0.2292 **0.2285** ±0.0022
25% blend 3 samples **Average** Stand. deviation	0.1603 0.1672 0.1658	0.1280 0.1335 0.1324	0.3439 0.3639 0.3561	0.1279 0.1332 0.1319	0.2409 0.2361 0.2394 **0.2388** ±0.0024
30% blend 3 samples **Average** Stand. deviation	0.1587 0.1589 0.1683	0.1274 0.1276 0.1351	0.3461 0.3445 0.3601	0.1271 0.1270 0.1341	0.2112 0.2119 0.2144 **0.2125** ±0.0017
100% DeVulCO"2 3 samples **Average** Stand. deviation	0.1777 0.2023 0.2000	0.1585 0.1805 0.1784	0.4298 0.4921 0.4923	0.1585 0.1799 0.1782	0.2047 0.2021 0.1988 **0.2022** ±0.0024
100% DeVulCO"2 (un-vulcanised) **Average** Stand. deviation	0.1679 0.1645 0.1698	0.1469 0.1439 0.1486	0.5234 0.4920 0.5241	0.1389 0.1307 0.1344	0.1509 0.1478 0.1415 **0.1467** ±0.0048

Sol and Volume fraction of swollen rubber

The amount of sol or rubber unconnected to the rubber network was calculated as the difference between the deswollen weight (m_d) in toluene and dry weight after the acetone extraction (m_e) and the observed trends in the results have been illustrated in Fig. 5.39.

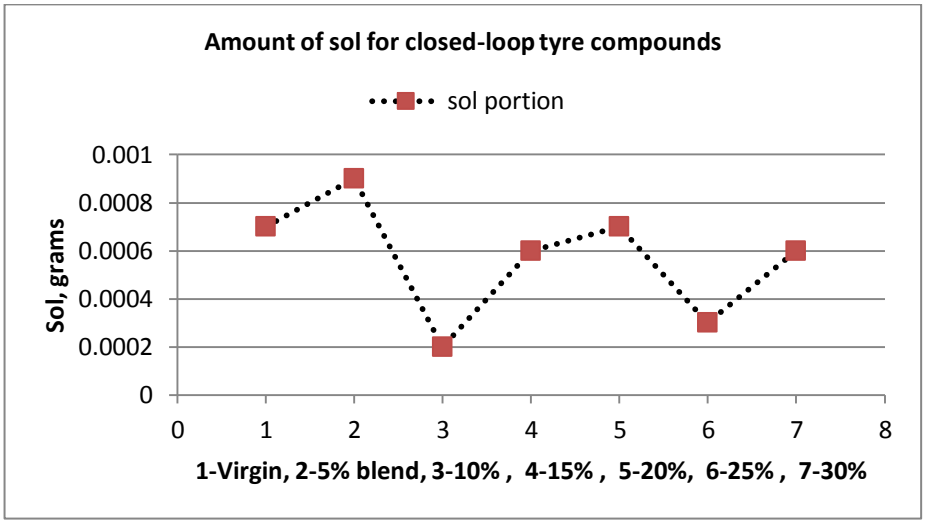


Fig. 5.39 Amount of sol for closed-loop tyre compounds

The amount of sol appeared to slightly increase with initial addition of DeVulCO"2 (5% blend) but decreased in the case of 10% blend and 25% blend. The values for the rest of the blends (15%, 20% and 30%) differed slightly from one another and were quite close to the value of the virgin compound (0.0007±0.0002). The sol fraction, which is the ratio of the amount of sol to the weight of dry sample after the acetone extraction, showed a similar trend and has therefore not been included here.

The amount of sol, expressed as sol fraction has been reported[85] to measure the effectiveness of the de-vulcanisation process carried out in a twin-screw extruder using EPDM rubber. Changes in de-vulcanisation conditions such as barrel temperature, screw speed and the amount of de-vulcanisation agent have been correlated to the amount of sol. A greater value of sol fraction was attributed to the high effectiveness of the de-vulcanisation process to remove cross-links.

As the closed-loop tyre compounds used in this study were based on the same DeVulCO"2 material it was not expected to see major changes in the amount of sol that are attributed to variations in the de-vulcanisation conditions. As the amount of sol can also be affected by the degradation of rubber during processing, the observed changes in the amount of sol in this study are more likely to be related to the processing conditions during blending.

However as shown in Fig. 5.40, the amount of sol for un-vulcanised 100% DeVulCO"2 greatly increased compared to the virgin compound and re-vulcanised DeVulCO"2. As the amount of sol is indicative of effective breakdown of polymer chains, the increased amount of sol can be related

to cross-link breaking during the de-vulcanisation process and subsequent cross-link formation on re-vulcanisation.

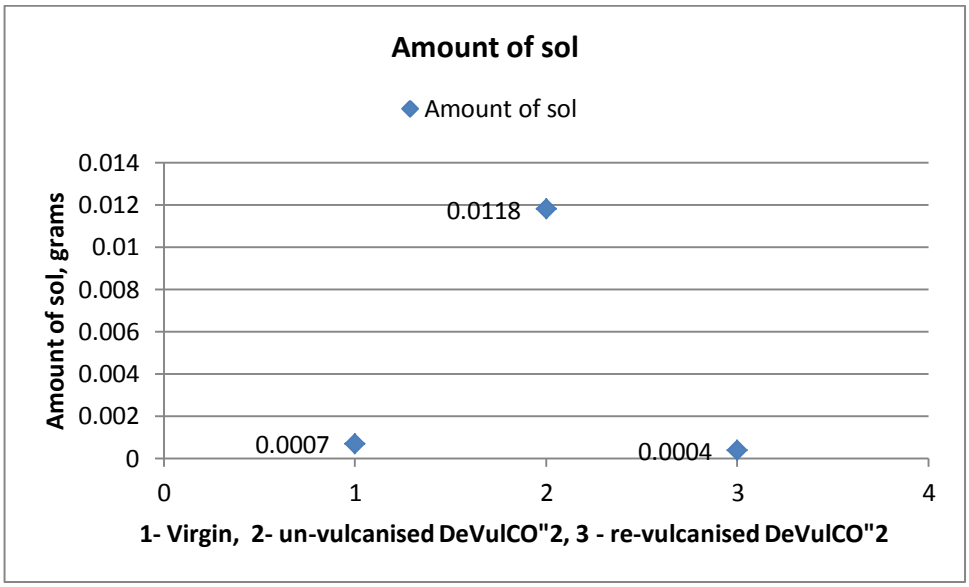


Fig. 5.40 Amount of sol for virgin and de-vulcanised closed-loop tyre compounds

The results of the volume fraction of rubber in swollen vulcanisate for virgin material and blends have been presented in Fig. 5.41. In this study the volume fraction has been used to indicate the amount of change in cross-link density. The volume fraction appeared to slightly increase with the initial addition of DeVulCO"2 and then attain a similar value, except for the 10% and 30% blends when the volume fraction decreased. The volume fraction of swollen rubber is related to the physically effective cross-link density and hence, moderate changes in its value would indicate similar moderate changes in cross-link density and similarity in properties.

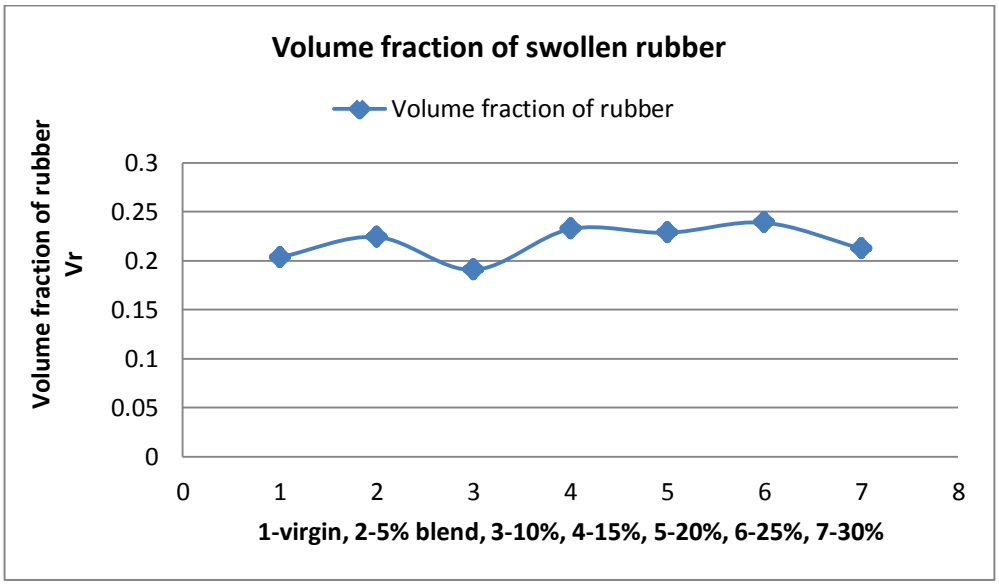


Fig. 5.41 Volume fraction of swollen rubber for closed-loop tyre compounds

The volume fraction of virgin compound was also compared to the un-vulcanised 100% DeVulCO"2

and re-vulcanised DeVulCO"2 compounds. It is clear from Fig. 5.42 that the volume fraction of un-vulcanised DeVulCO"2 is lower than the value for virgin material. However, the volume fraction of the re-vulcanised DeVulCO"2 appeared to be comparable to the virgin compound. The reduced value of the volume fraction of swollen de-vulcanisate indicates the reduction in the cross-link density as a result of de-vulcanisation.

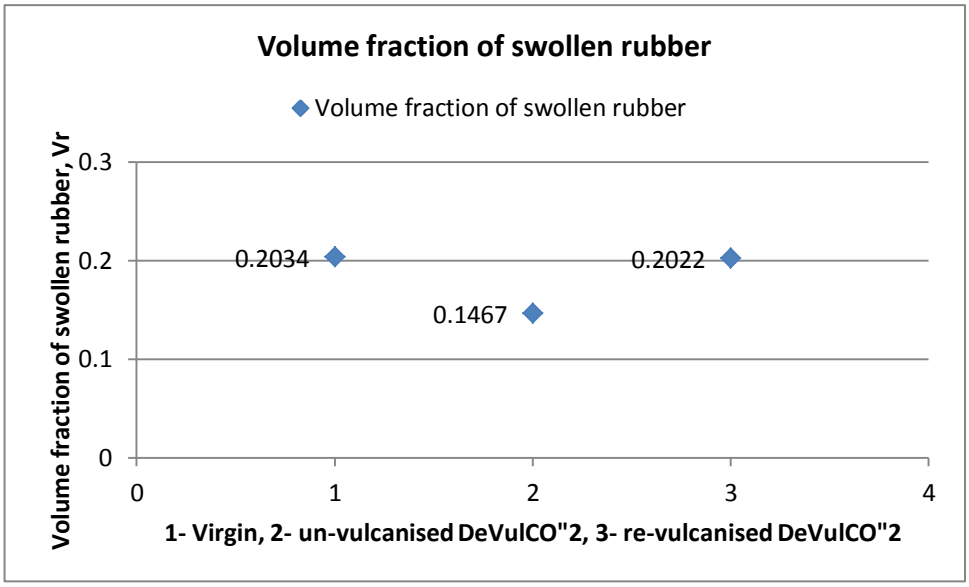


Fig. 5.42 Volume fraction of virgin and de-vulcanised closed-loop tyre compounds

The results of volume fraction for virgin compound and blends were compared to the results of the Mooney Viscosity (Fig. 5.43). In both cases minor changes were observed between the blends and the virgin material, possibly due to the dominant effect of virgin material in the blends. However, in both cases a significant difference was observed between the results for un-vulcanised DeVulCO"2 and virgin material, as shown in Fig. 5.1 and Fig. 5.42.

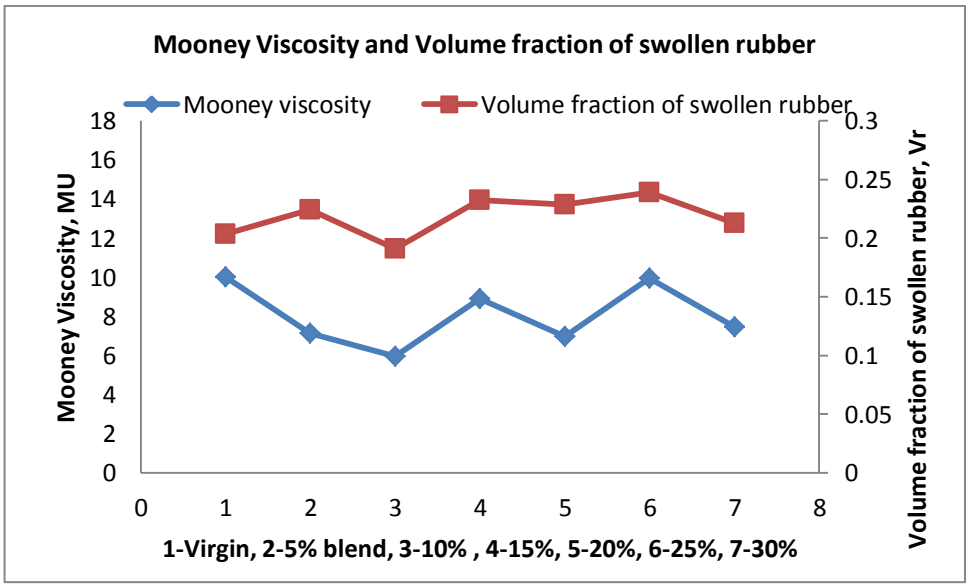


Fig. 5.43 Mooney viscosity and volume fraction values for closed-loop tyre compounds

To sum up, the following conclusions have been drawn from the results of the swelling measurements:

Amount of sol

- The values of sol in closed-loop tyre blends were similar to one another and to the virgin material, except for 10% and 25% blends that could have been affected by processing conditions during blending.
- The amount of sol for un-vulcanised DeVulCO"2 was significantly higher than for the blends and the virgin material, indicating cross-link breaking caused by de-vulcanisation.
- The amount of sol for un-vulcanised DeVulCO"2 significantly decreased on re-vulcanisation and became comparable to the values of blends and virgin material, indicating cross-linking taking place on re-vulcanisation.

Volume fraction of rubber in swollen vulcanisate

- The values of the volume fraction in closed-loop tyre blends were similar to one another and to the virgin material, except for 10% and 30% blends that were slightly lower.
- The value of volume fraction for un-vulcanised DeVulCO"2 was lower than for the blends and virgin material, indicating a network reduction following the de-vulcanisation process. The value of volume fraction for re-vulcanised DeVulCO"2 was comparable to the value of virgin compound and the blends.
- A similar trend in the results has been evident between the volume fraction and Mooney viscosity for the closed-loop blends. In addition, some similarities have been observed between torque rise and volume fraction (except for 30% blend).

5.4 FTIR spectroscopy

General applications of the FTIR spectroscopy to characterise polymers were outlined in section 3.6 (Spectroscopic techniques) of Chapter 3. A review[40,94,95,123,124] of applications of the FTIR spectroscopy to characterise de-vulcanised and re-vulcanised waste rubbers showed that it is mainly used to compare chemical composition of de-vulcanised, re-vulcanised and virgin rubbers. Traditional infrared spectroscopy usually requires sample preparation and on its own does not appear to be sensitive enough to guide optimisation of the de-vulcanisation process by detecting relevant structural changes. However, FTIR using ATR requires minimum sample preparation and may provide a useful tool to identify polymer composition and compare the consistency of recycled material prior to de-vulcanisation, particularly in the case of ELT.

As explained in Chapter 4 (Experimental work) selected rubber samples were analysed using FTIR Nicolet 380 Spectrometer with an ATR attachment that was equipped with a diamond crystal and coupled with Omnic software. During the experimental work, a variety of rubber samples were analysed: in crumb form and milled into a sheet; un-vulcanised and vulcanised; as received and extracted with acetone to remove non-rubber components. In this work, the spectrum wavenumber

range of 4000-400 cm^{-1} (mid-infrared region) was employed. However, the most relevant range of the spectrum, the fingerprint region (1450-600 cm^{-1}), was then selected to support discussion in this section.

Waste Rubber Crumb

FTIR spectroscopy is a useful tool in determining the polymer composition of rubber material and hence, can be particularly beneficial to check the consistency of waste rubber crumb that often comes from multiple sources.

The consistency of 40 mesh tyre crumb, supplied by J.Allcock & Sons (Fig.4.1, Chapter 4) for use in the initial de-vulcanisation studies of the project work was characterised by the FTIR spectrometer. Six samples were taken at random from a 10 kg batch and analysed as received. Their spectra are presented in Fig. 5.4.1. It can be seen in Fig. 5.4.1 that all six spectra over the selected range of wavenumber (1100-500 cm^{-1}) are very similar and superimposable, showing that all samples have a similar molecular structure.

De-vulcanised Waste Rubber Crumb

Similarly, the consistency of the de-vulcanised tyre crumb was also evaluated. These samples were first re-vulcanised and then characterised by the spectrometer. Their spectra over the selected range of wavenumber (1140-600 cm^{-1}) have been presented in Fig. 5.4.2. It is clear from Fig. 5.4.2 that de-vulcanised samples have similar and superimposable spectra and hence, similar molecular structure. Establishing a good consistency within the samples was important as it allowed a meaningful comparison between the waste rubber crumb and de-vulcanised sample, originated from the same source.

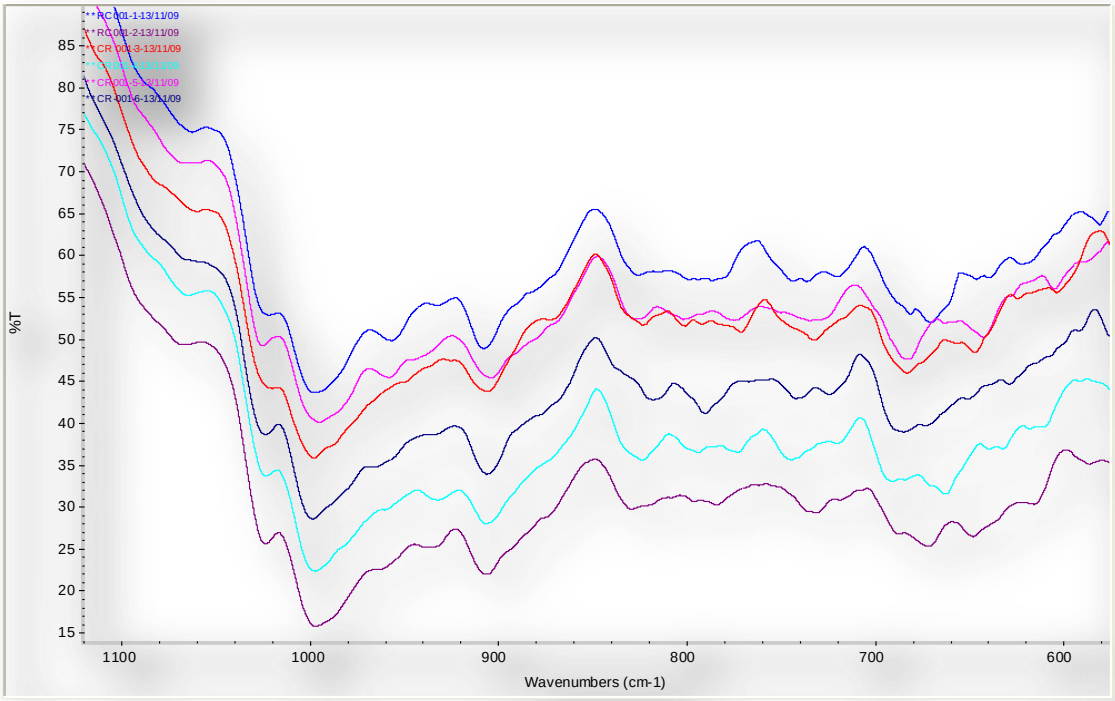


Fig. 5.4.1 Offset IR Spectra (1100-500 cm^{-1}) of ELT crumb taken by random sampling

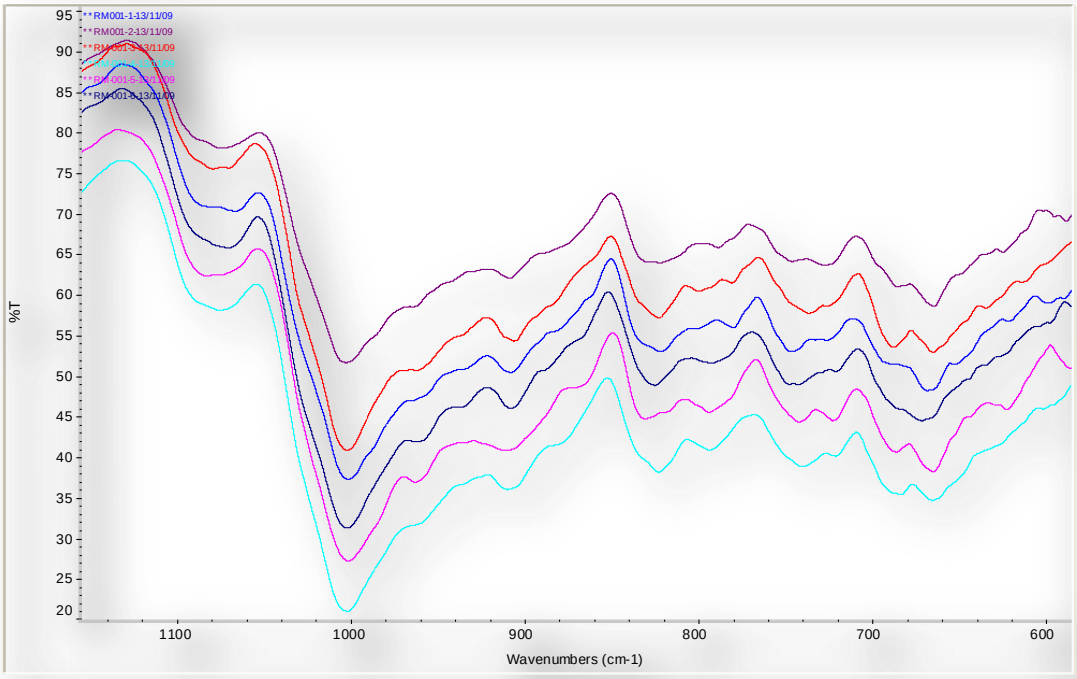


Fig. 5.4.2 Offset IR Spectra (1140-600 cm^{-1}) of six de-vulcanised samples originated from ELT crumb

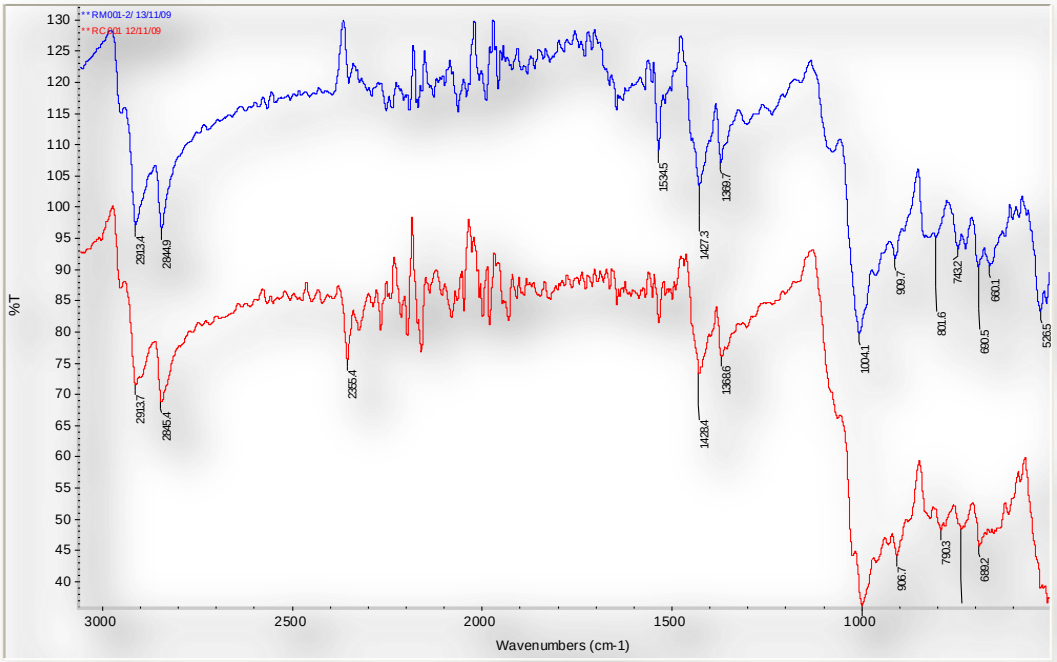


Fig. 5.4.3 Offset IR Spectra (3000-500 cm $^{-1}$) of original (red) and de-vulcanised (blue) rubber crumb

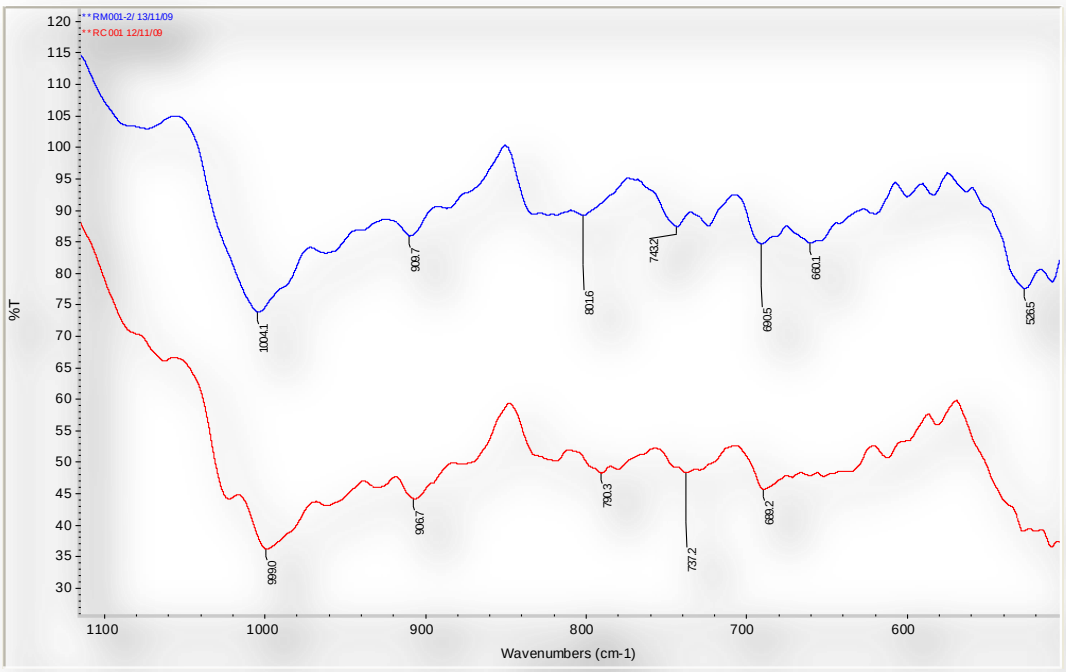


Fig. 5.4.4 Offset IR Spectra (1100-500 cm^{-1}) of original (red) and de-vulcanised (blue) rubber crumb

The infrared spectra of the original ELT and de-vulcanised and subsequently re-vulcanised waste

tyre crumb are shown in Fig. 5.4.3 and 5.4.4. It is evident from the spectra of the two samples in Fig. 5.4.4 that they are very similar but not entirely superimposable. Apart from a slight difference in the 800-790 cm^{-1} region that is consistent with that observed with the six random samples (Fig. 5.4.1), there is a developed band in the de-vulcanised sample at 1075 cm^{-1} compared to a shoulder in the original sample. In addition, a shoulder band present in the original crumb at 1025 cm^{-1} disappears in the de-vulcanised sample. Although, the peak at 1076 cm^{-1} has been attributed to C-S-C group stretching vibrations in the two C-S bonds in vulcanised NR[181] and peak at 1029 cm^{-1} to C-S bonds[182], the observed minor differences between the original ELT crumb and de-vulcanised material do not appear strong enough to guide optimisation of the de-vulcanisation process.

Fig. 5.4.1 and Fig. 5.4.2 confirmed the practicality of using ATR-FTIR for evaluating the consistency of the incoming waste ELT crumb and de-vulcanised material, but in addition the results presented in Fig. 5.4.3 confirmed that ATR-FTIR can also be used to establish the approximate polymer composition. The infrared spectra of the original ELT crumb and de-vulcanised material are clearly showing characteristic peaks in the 3000-2850 cm^{-1} region and approximately at 1450 cm^{-1},1375 cm^{-1} and 886 cm^{-1} that are indicative of NR[120,183]. While the existence of the peaks at around 700 cm^{-1} and 996 cm^{-1} can be assigned to the presence of the SBR and BR components respectively[40].

Closed-loop tyre blends

To eliminate possible errors in the FTIR results caused by contamination and/or inconsistency of the waste tyre crumb, the closed-loop tyre materials (Table 4.1, Chapter 4) have been used in further analysis. Vulcanised samples were first extracted with acetone to remove non-rubber components and the liquid portion (acetone extract) of the blend was analysed and compared to virgin material. The spectra of the analysed samples are given in Fig. 5.4.5 to Fig. 5.4.9.

The extracted solid samples (residue) were also analysed by the spectrometer and their spectra have been presented in Fig. 5.4.11.

Extracted Closed-loop Tyre Samples (Acetone extract)

In general, finding an absorption range where common rubber additives show strong absorption peaks is difficult due to the low concentration of additives in rubber[184]. Another challenge comes from overlapping bands that come from the polymer and solvent.

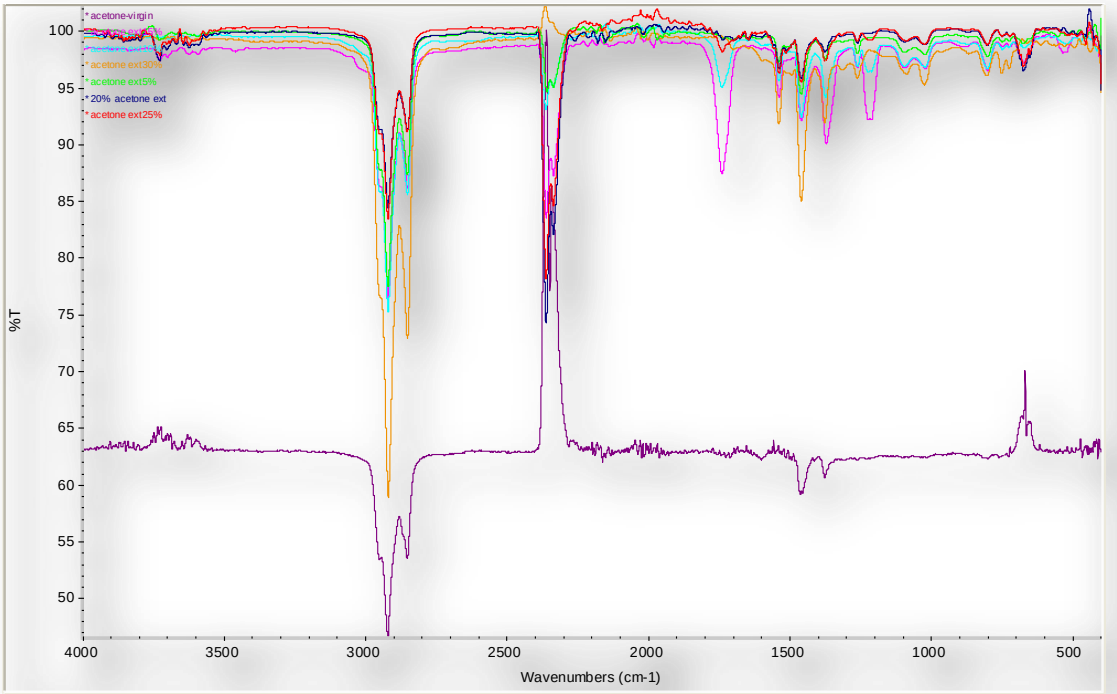


Fig. 5.4.5 IR Spectra of the acetone extracts for closed-loop tyre blends (top) and virgin sample (bottom)

Examination of the spectra in Fig. 5.4.5 over the range of 4000-500 cm^{-1} revealed strong similarities between the acetone extracts of the blends. However, the spectra of the blends exhibited a number of differences to the virgin sample, particularly between 1900 cm^{-1} and 600 cm^{-1}.

All extracts would expect to show some presence of non-rubber additives[184] (e.g. activators, accelerators, sulphur, mineral oil, fatty acids) and acetone in their spectra and hence, the spectrum of acetone, used for extraction, was included for comparison in Fig. 5.4.6 and Fig. 5.4.7. Comparison of the spectra in Fig. 5.4.6 indicated that the difference in the spectra of the blends and virgin material may be due to incomplete removal of acetone, as evident from the strong acetone-related bands in the blends at approximately 1710 cm^{-1}, 1450 cm^{-1}, 1357cm^{-1}, 1219 cm^{-1}, 1093 cm^{-1}, 903 cm^{-1}, 780 cm^{-1} and 531 cm^{-1}. Apart from the acetone-related peaks, it has been noticed that a well resolved peak at around 1540 cm^{-1} is present in the spectra of all the blends and is clearly absent in the virgin sample and acetone.

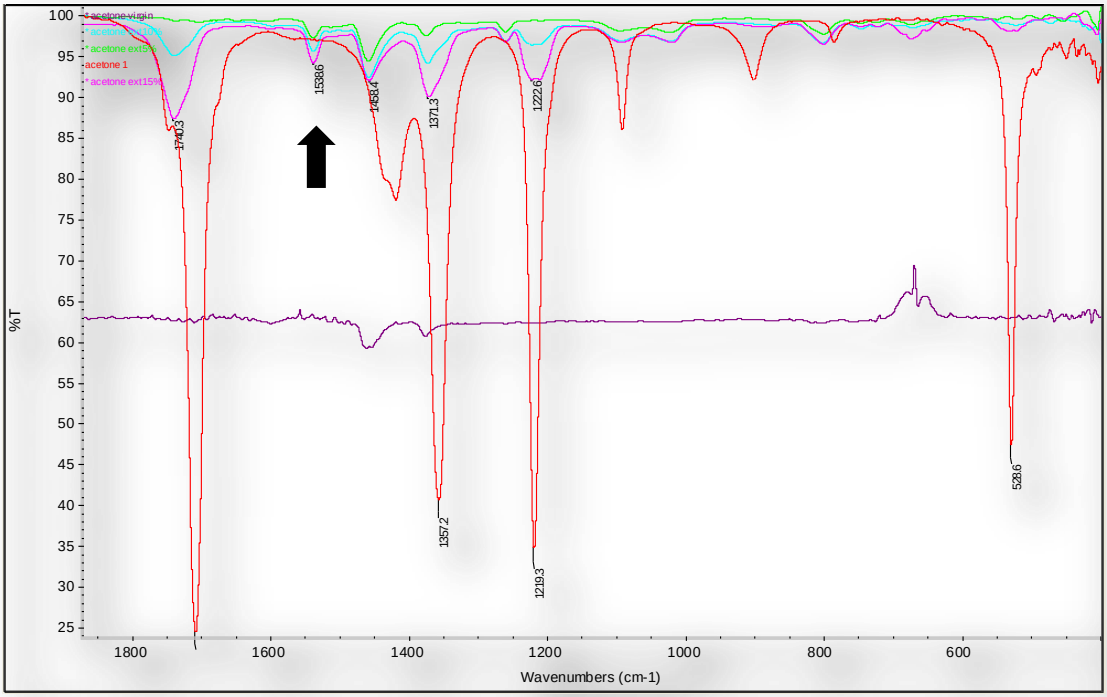


Fig. 5.4.6 IR Spectra (1900-400 cm $^{-1}$) of acetone (red) and extracts of virgin sample and selected closed-loop blends

Further examination of the peak in Fig. 5.4.7 and 5.4.8, showed that its intensity appeared to increase with additions of DeVulCO"2 content of 5%, 10% and 15%. As illustrated in Fig. 5.4.9, the intensity of the peak continued to increase at 30% addition. However, it seemed to decrease significantly for 20% addition before increasing again for 25% addition. Overall, the following pattern in the intensity of the peak has been observed:

5% → (20% → 25%) → 10% → 15% → 30% (visually observed trend)

To confirm the observed trend, the peak area corresponding to the peak at 1540 cm^{-1} was measured using the FTIR software. As the peak area is directly proportional to the thickness or concentration of the sample, the peak area method has been reported by G. Tao et al[185] to analyse the structural changes in de-vulcanised by mechanical shear waste tyre crumb.

To ensure the accuracy of the results, the area corresponding to the peak at 1540 cm^{-1} was measured over the same wavenumber range (1560 cm^{-1} – 1520 cm^{-1}) for all samples. The results of the measurements have been presented in Table 5.4.1 and Fig. 5.4.10 and clearly confirm the trend visually observed from the spectra of the blends.

The acetone related peak at around 1375 cm^{-1} which is present in all extracts (virgin and blends) was selected as an internal standard. The peak area of the internal standard was measured using

the same technique as for 1540 cm^{-1} peak. The selected wavenumber range for this peak area was between 1396 cm^{-1} and 1356 cm^{-1}. The absorption peak areas at 1540 cm^{-1}, 1375 cm^{-1} and their ratio are presented in Table 5.4.1.

Table 5.4.1 Absorption peak areas and their ratio at 1540 cm^{-1} and 1375 cm^{-1}

Sample Closed-loop tyre	Description	Peak area at 1540 cm^{-1}	Peak area at 1375 cm^{-1}	Peaks area ratio (1540/1375)
1	5% blend	0.1322	0.1095	1.21
2	10% blend	0.2079	0.2298	0.9
3	15% blend	0.2830	0.3650	0.8
4	20% blend	0.1361	0.0791	1.72
5	25% blend	0.1462	0.1233	1.19
6	30% blend	0.3977	0.3659	1.10

It is evident from Table 5.4.1 that the absorption peak area for both peaks changes from sample to sample, following the same trend in both cases. As a result, the peak area ratio values are very close (approximately equal to 1) for all samples excluding the 20% blend extract sample.

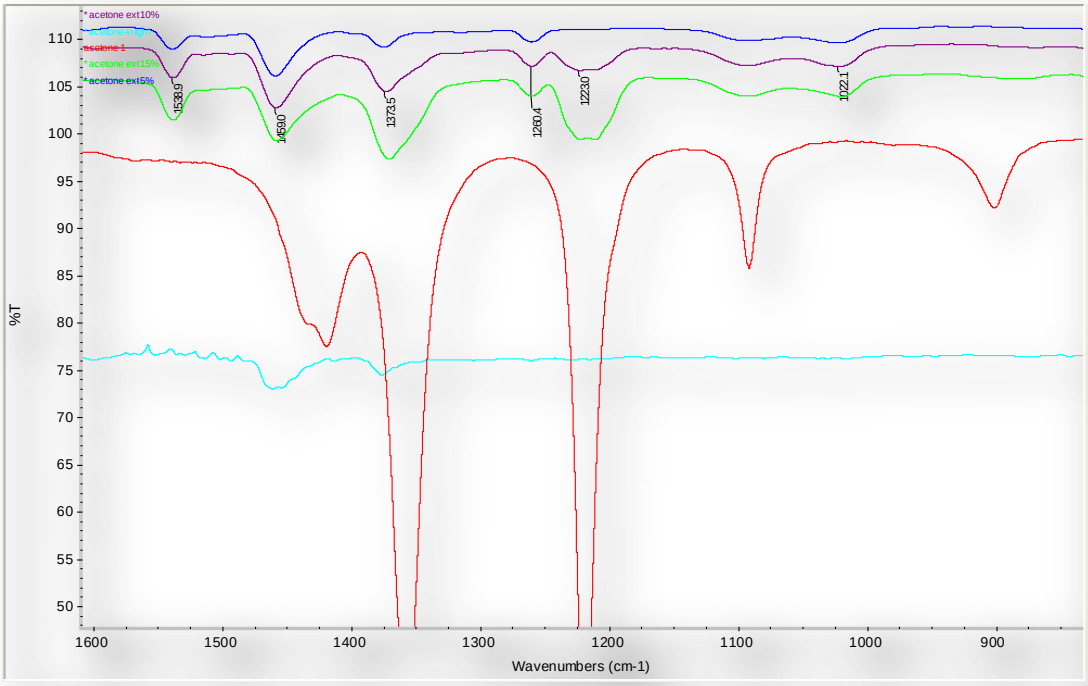


Fig. 5.4.7 Offset IR Spectra (1600-800 cm^{-1}) of acetone (red) and extracts of virgin sample and selected closed-loop blends

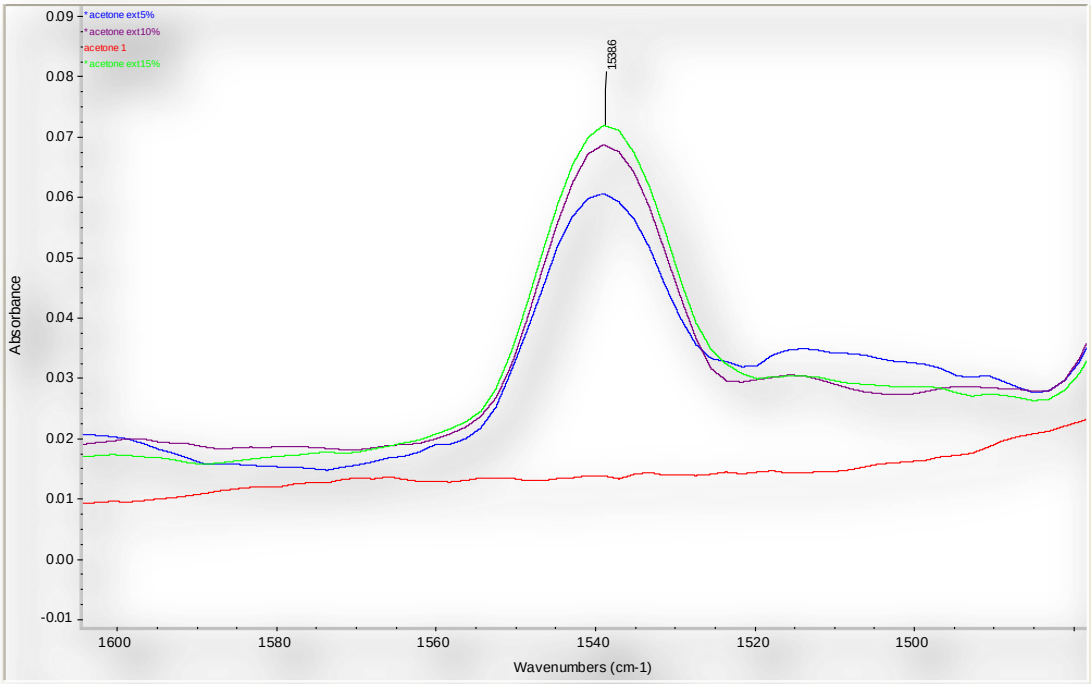


Fig. 5.4.8 Peaks at 1540 cm^{-1} for selected closed-loop tyre blends and acetone (red)

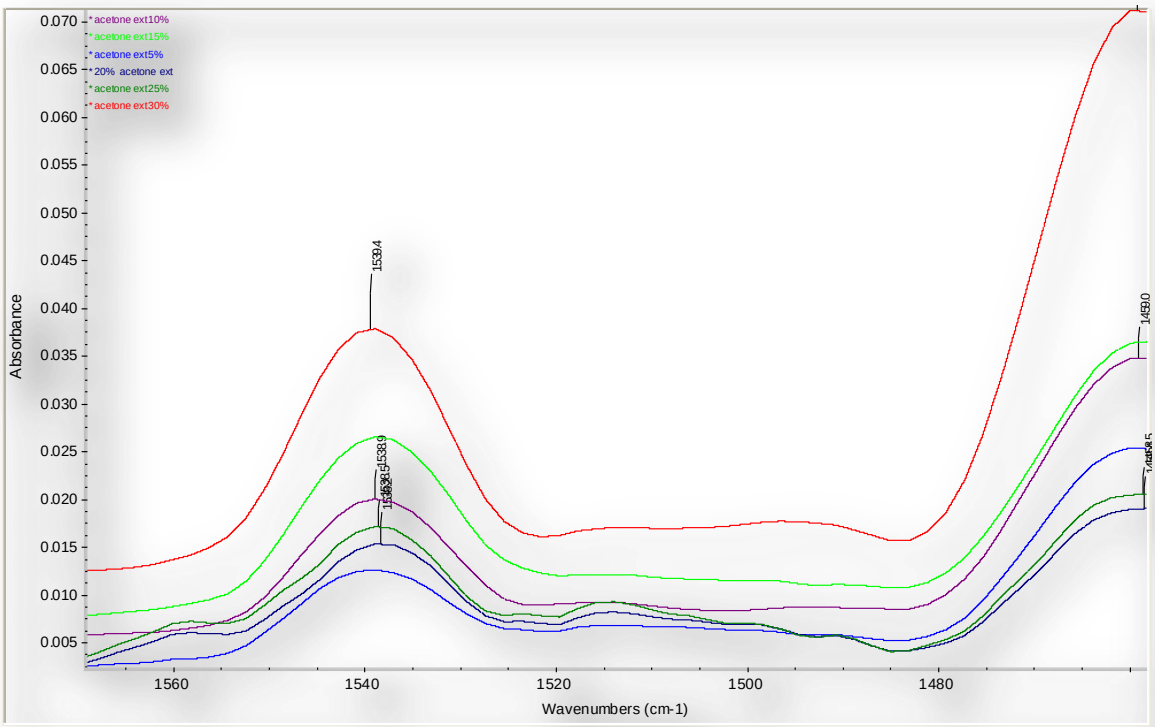


Fig. 5.4.9 Difference in intensity at 1540cm^{-1} for closed-loop tyre blends

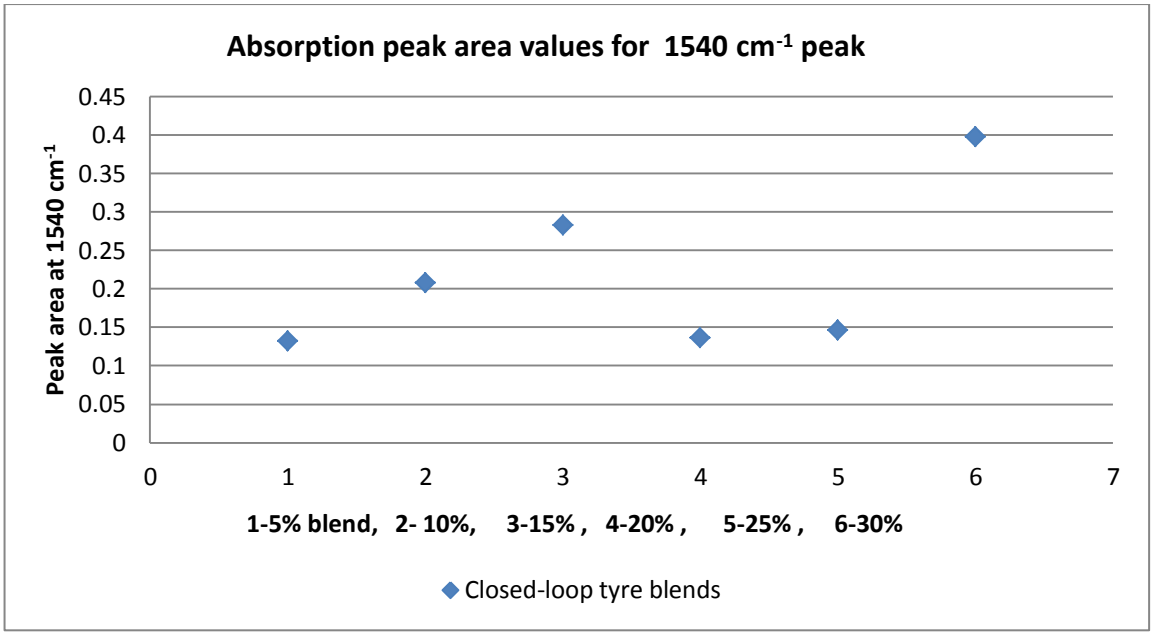


Fig. 5.4.10 Absorption peak area values at 1540 cm^{-1} for closed-loop tyre blends

Rubber extracts contain a large amount of chemicals that are often difficult to distinguish by the FTIR alone due to their low concentration and weak and/or overlapping signals. The absorption peak at 1540 cm^{-1} could be related to the presence of ZnO[186,187]. Zinc oxide is expected to be employed during both, vulcanisation and de-vulcanisation processes, in the case of closed-loop tyre materials, as a vulcanisation activator and a de-vulcanisation agent respectively. The peaks of the other chemicals or their residues that are relevant to vulcanisation/de-vulcanisation (e.g MBTS, ZDEC, TBBS) would be expected in the region of 1540-600 cm^{-1} but apart from the peak at 1540 cm^{-1} are difficult to confirm due to the overlapping acetone peaks.

Extracted Closed-loop Tyre Samples (Residue)

The closed-loop tyre materials extracted by acetone (residue) were also analysed by the spectrometer and the spectra of the blends and virgin sample are presented in Fig. 4.5.11. The spectra of all samples do not appear to have clearly resolved peaks for characterisation. This is likely to be as a result of the carbon black reinforced filler present in all materials.

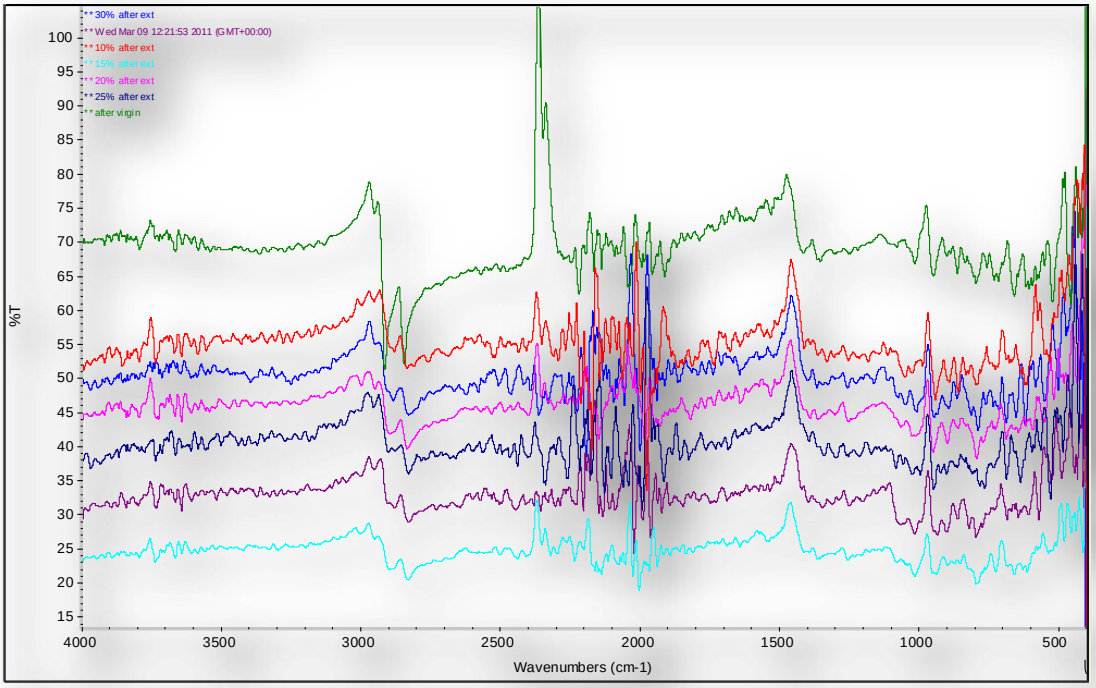


Fig. 5.4.11 IR Spectra (4000-500 cm^{-1}) of the residue for extracted closed-loop samples: blends and virgin material

The following conclusions were drawn from the FTIR results:

- FTIR-ATR requires minimum sample preparation and proved useful in studying the consistency and polymer composition of incoming recycled material.
- Although some differences were observed between the spectrum of the original and de-vulcanised rubber crumb, they did not appear to be significant enough to guide optimisation of the de-vulcanisation process.
- The acetone extracts of the closed-loop tyre compounds containing DeVulCO”2 showed an emerged peak at around 1540 cm^{-1}. However, quantitative analysis of the peak area did not establish any useful outcomes that can be related to the de-vulcanisation study.
- The residue of the closed-loop tyre compounds did not have enough resolved peaks in the spectra to be useful.

5.5 NMR spectroscopy

Nuclear Magnetic Resonance spectroscopy is a useful characterisation tool for analysing polymer structure. In this context its most important use has been to study the mobility of polymer chains and hence the network characterisation. A detailed review of NMR spectroscopy and how it can be used for cross-linking studies of rubbers is provided in section 3.6 (Spectroscopic techniques) of Chapter 3. The outcome of this review identified the swollen state proton NMR technique (swollen state ^{1}H-NMR), developed by Tinker and co-workers[130,132,133], as the most relevant and promising

technique for cross-linking studies of the de-vulcanised and re-vulcanised ELT. As highlighted in the literature review, the technique has been successfully applied to a wide range of elastomers, their blends and carbon black filled compounds. Although, it does not provide a direct measurement of cross-link density, the data obtained by this technique can be correlated to the cross-link density and/or its indicators (e.g. V_r or rheometer torque characteristics) obtained by other techniques. Moreover, this technique does not require a special set up of the NMR instrument or use of special devices and is simple to analyse. In this study the swollen state ^{1}H-NMR technique has been extended to characterise the rubber network of de-vulcanised and re-vulcanised ELT materials.

To obtain a high resolution NMR spectrum a solid polymer sample has to be first dissolved in an appropriate solvent. However, some polymers, including rubbers, do not dissolve but rather swell due to their cross-linked structure. The specialised swollen state ^{1}H-NMR technique is based on a relationship between the peak broadening in the spectra of swollen vulcanisates and their cross-link density. The commonly used method to measure peak width is to determine the signal width at half peak height. However, this approach is not suitable for analysing the ^{1}H-NMR spectra due to insufficiently-resolved and overlapping signals[131]. As explained in section 3.6 (Spectroscopic techniques) of Chapter 3, one of the most important parameters in the swollen state ^{1}H-NMR technique is H%. This parameter increases as the peak broadens, corresponding to an increase in cross-link density and hence, can be used to define the width of the peak. Selected closed-loop tyre materials (Table 4.3, Chapter 4) were prepared and analysed by the specialised swollen state ^{1}H-NMR technique as detailed in section 4.6 (NMR spectroscopy) of Chapter 4.

Data analysis:

The spectra of the closed-loop tyre materials are included in Fig. 4.12 to Fig.4.15 and the spectra of the extracts of the virgin material and the corresponding de-vulcanised rubber crumb are given in Fig. 4.16 and Fig.4.17 respectively. These two sets of data have been discussed separately in the rest of this section. Each spectrum shows intensity of an NMR signal (y-axis) as a function of chemical shift (x-axis). Chemical shift is expressed in parts per million (ppm) and is a measure of how far the signal produced from the proton is from the reference material, TSM. A detailed explanation of the axes is provided in section 3.6 Spectroscopic techniques (Chapter 3).

Closed-loop tyre samples (Gel):

In order to calculate the peak width parameter, H% the spectra of the closed-loop tyre materials were examined to identify a suitable peak for analysis. All samples showed the same main signals and the spectrum in Fig. 5.5.1 is used as an example to illustrate the main peaks. The peaks at 0 ppm (TSM) and 7.26 ppm ($CDCl_3$) were assigned to the solvents and appeared to be skewed to the downfield side of the peak. This is likely to have been caused by the presence of secondary signals arising from the TSM or chloroform within the swollen vulcanisate that are positioned just downfield of the primary signals. It is interesting to note that there is no evidence of aromatic

proton signals in the region of the chloroform signal that would normally indicate the presence of the SBR. This must be due to the absence or very small amount of SBR in the present tyre composition. A number of peaks in the aliphatic region of the spectrum (2 to 1 ppm) can be assigned to the methylene (CH_2) and methyl (CH_3) protons of the NR, BR and SBR components of the tyre blend material. The fairly broad olefinic signal, observed at around 5.12 ppm, can be assigned to the methine (CH) protons and is generally the most suitable[131] for measurements performed on unsaturated elastomers. Therefore, the olefinic peak of the spectrum was selected to calculate the H% parameter in the closed-loop tyre materials. Small peaks observed on the olefinic peak in some of the samples (15% and 25% blends) were likely to have been caused by the presence of some residual small molecules in the vulcanisate and were ignored.

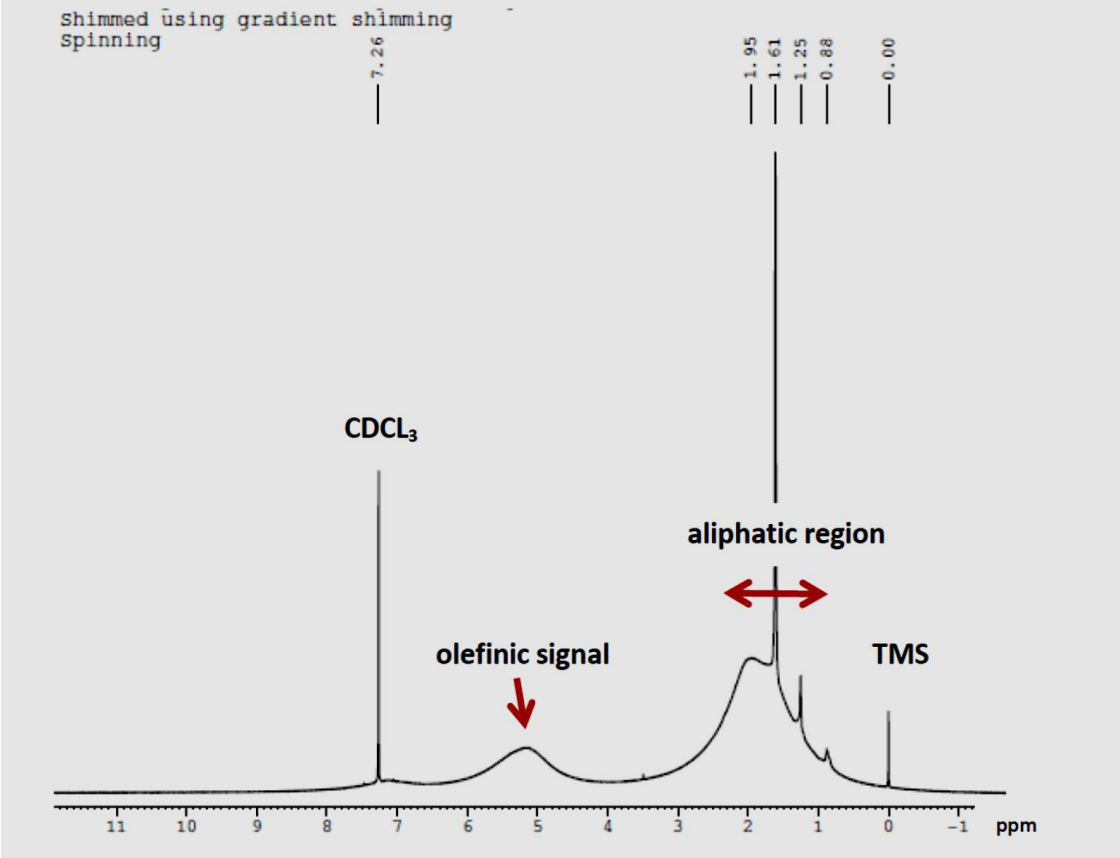


Fig. 5.5.1 ^{1}H- NMR spectrum of the virgin closed-loop tyre material

Determination of the H% parameter:

First of all, the spectrum data (intensity and frequency relative to TMS in Hz) of each sample was imported to Microsoft Excel. The frequencies in Hz were then converted to ppm by dividing their values by the spectrometer frequency in MHz (500.13 MHz). The position of the reference point is arbitrary and is selected on the basis that H% should provide good discrimination between the materials used[130]. Considering the broadness of the olefinic peaks of all samples, the reference point was selected as 0.6 ppm downfield from the olefinic peak frequency. The excel data was then used to determine the peak of the olefinic signal (point B) as shown in Fig. 5.2.2 and the

corresponding chemical shift value and intensity. The chemical shift value of the peak at point B was then used to find the coordinates of point A and hence, to calculate the parameter H%.

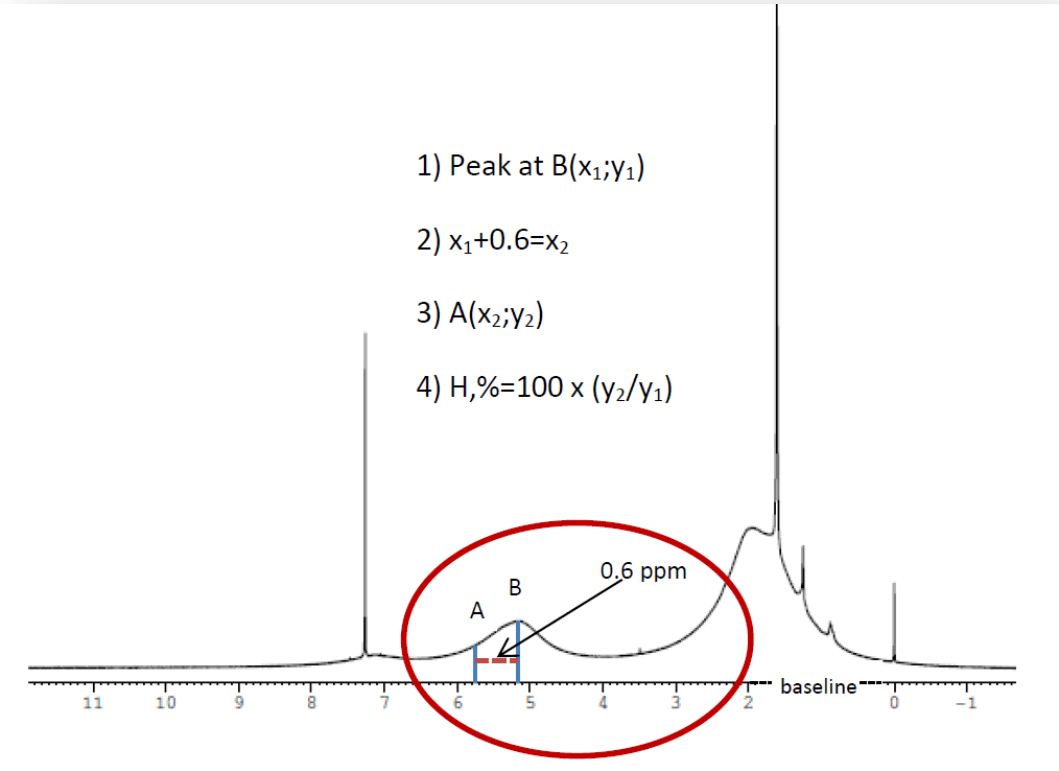


Fig. 5.5.2 ^{1}H- NMR spectrum of virgin closed-loop tyre material and the H,% parameter

Therefore, the width of the olefinic peak H% has been defined by the signal strength at a position on the side of the peak (0.6 ppm downfield from the peak position) expressed as a percentage of the peak signal strength. The values of H% for the closed-loop tyre materials have been given in Table 5.5.1

Table 5.5.1 Results of H% for re-vulcanised closed loop tyre materials

Sample	**Truck Tyre Virgin rubber, %**	**DeVulCO"2 Truck Tyre crumb, %**	**Parameter, H %**
Virgin rubber	100%	0%	44.19
15% blend	85%	15%	58.94
25% blend	75%	25%	64.67
30% blend	70%	30%	71.16

The values of the parameter H% in Table 5.5.1 show an increase in the width of the olefinic peak with the addition and increased percentage of de-vulcanised material. As the greater signal width is associated with the lower mobility of a vulcanisate, swollen in an appropriate solvent, and increased cross-linking, these results indicate an increase in the cross-link density with the addition of increasing amounts of DeVulCO"2 in the blends.

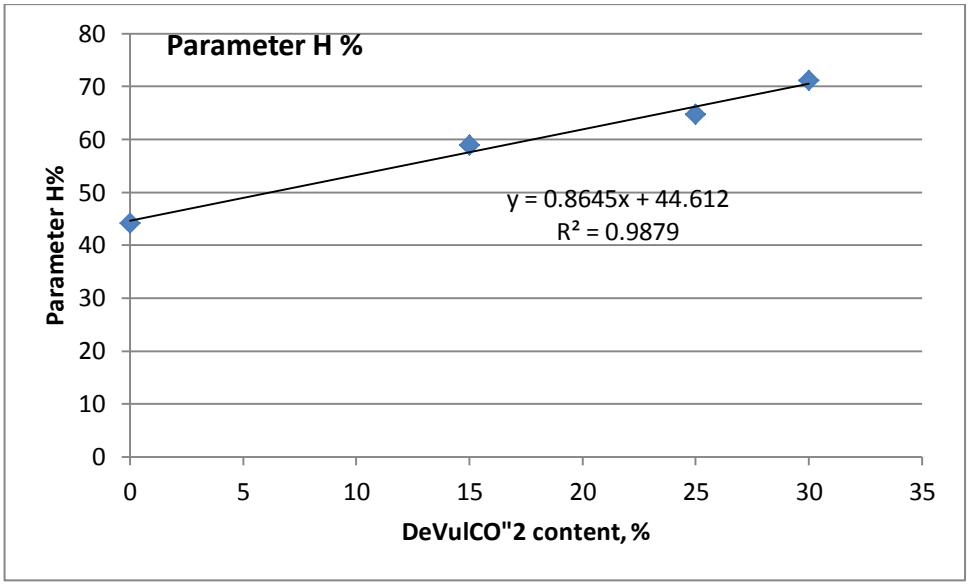


Fig. 5.5.3 Influence of de-vulcanisate loading on H% for closed-loop tyre compounds

A linear increase in H% with a high correlation coefficient (R^2=0.9879) is observed with increase in DeVulCO"2 content as evident from Fig.5.5.3.

The results of the width of the peak for closed-loop tyre materials were then considered in relation to other parameters relevant to the de-vulcanisation process (e.g. Mooney viscosity, relevant curing characteristics and swelling measurements).

Mooney viscosity and Mooney relaxation:

Values of the Mooney viscosity of the closed-loop tyre blends were quite similar to the virgin material (8±2 MU). The Mooney relaxation parameters (e.g. $M_{ret.30s}$) may have afforded a better comparison, as it relates to the elastic component of un-vulcanised material. However, the Mooney relaxation parameters were not determined for the closed-loop materials for the reasons explained earlier.

Curing characteristics:

The results of H% parameter are in good agreement with the curing characteristics, relevant to the de-vulcanisation process: the minimum torque (M_L), the maximum torque (M_H), the torque rise (M_H-M_L) and the maximum cure rate. It can be seen from Table 5.5.2 that all parameters increase on addition of DeVulCO"2 and continue to increase as the amount of de-vulcanised material in the

blend is increased.

Table 5.5.2 Comparison of the selected curing parameters and H% for closed-loop tyre materials

Sample	Composition: amount of DeVulCO"2	H%	M_L, dN m	M_H, dN m	M_H-M_L, dN m	Max. cure rate, dN m min^{-1}
1	Virgin	44.19	6.50	49.50	43.00	10.00
2	15% blend	58.94	10.00	56.50	46.50	23.60
3	25% blend	64.67	14.50	61.50	47.00	27.30
4	30% blend	71.16	16.00	64.50	48.50	28.00

The minimum torque is related to the stiffness of the un-vulcanised rubber; increased values of the torque, M_L may indicate additional elastic contributions from the cross-links still remaining in the original rubber network. As the de-vulcanised material is already cross-linked to some extent, the maximum torque can provide a more relevant measure of cross-linking. Both, the maximum torque and parameter H% increased on addition and with increased amount of DeVulCO"2, indicating an increase in the total level of cross-linking. Moreover, a linear relationship (R^2=0.9869) appears to exist between these two parameters, as illustrated in Fig. 5.5.4, opening up the possibility of constructing a calibration plot relevant to the study of de-vulcanisation.

The torque rise corresponds to the amount of cross-links introduced and is also in good agreement with the results for H%. In addition, the maximum cure rate also provides a good indication of new cross-link formation and is in good agreement with the results of H%.

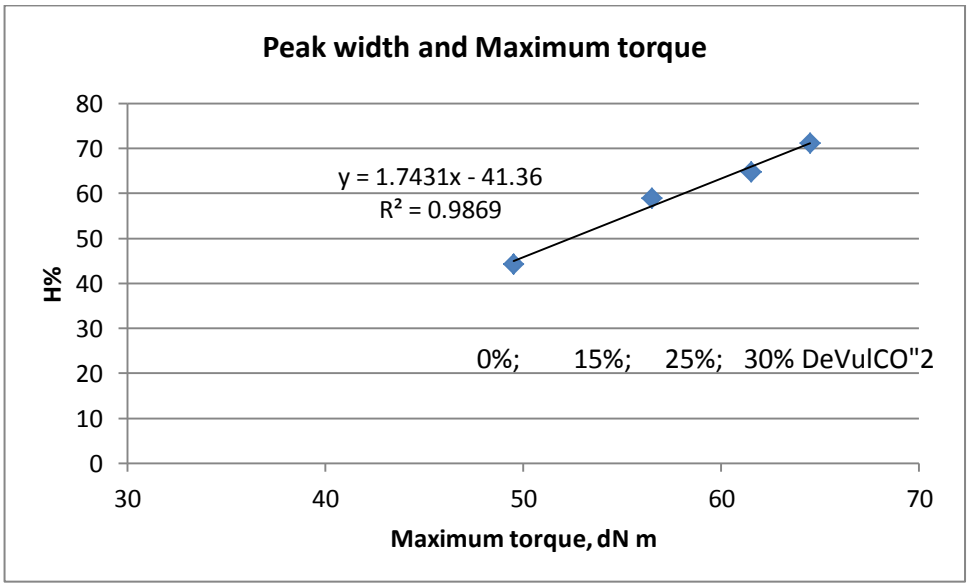


Fig. 5.5.4 Correlation between the peak width and maximum torque for closed-loop tyre materials

Swelling measurements:

The volume fraction of swollen rubber, V_r has been used in this work to characterise the rubber network as it relates to the physically effective cross-link density of rubber (equation 9, Chapter 3). Comparing the results of the olefinic peak broadening to the corresponding values of V_r (Fig. 5.5.5) reveal good agreement of the results except for the 30% blend sample. The determine whether the decreased value of V_r for this material was due to swelling measurement error, the results were reviewed alongside the mechanical properties in the next section of this chapter.

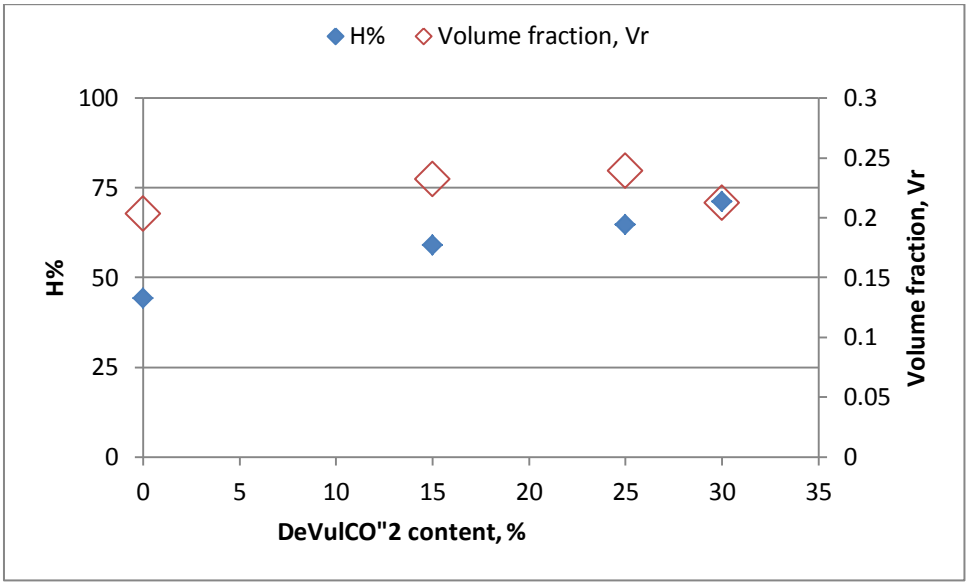


Fig.5.5.5 Influence of de-vulcanisate loading on parameters H% and V_r for closed-loop tyre materials

Virgin and DeVULCO"2 Extracts (Sol)

Due to the difficulties of using the NMR instrument to detect DeVulCO"2 in a crumb form, the swollen crumb extract was analysed instead and compared to the virgin material extract. The spectra of these materials revealed an important difference in the olefinic region at around 5.1ppm and 5.4 ppm that have been assigned to NR and cis-1.4 BR accordingly[134]. However, the broadness of the peak at around 5.4 ppm is particularly evident from the DeVulCO"2 spectrum, also suggesting the presence of the SBR[188]. The existence of these rubber components in the extract of de-vulcanised material can be related to de-vulcanisation efficiency as they are indicative of the sol fraction or proportion of polymer chains that are no longer connected to the main network of vulcanised rubber. As explained in Chapter 3 of this thesis, the amount of soluble material present as part of the extraction or swelling measurements can be quantified and related to the de-vulcanisation efficiency. However, these techniques do not distinguish between the contribution made to either the sol fraction from the cross-link breaking or the main chain breaking and are usually considered alongside other techniques. In general, a significant amount of sol present in de-vulcanised material is related to the high efficiency of the de-vulcanisation technique, that allows rubber to be re-vulcanised and re-processed[189].

The ^{1}H-NMR spectroscopy has been used in this study to identify and quantify the amount of soluble rubber components to indicate the efficiency of the de-vulcanisation process. As the closed-loop tyre materials are a blend of more than one rubber, the ratio of the area under the relevant olefinic peaks for each sample, before and after the de-vulcanisation process was compared to distinguish the efficiency of the de-vulcanisation process of each individual components of the blend.

The comparative spectra of both samples show distinct differences and is presented in Fig. 5.5.6.

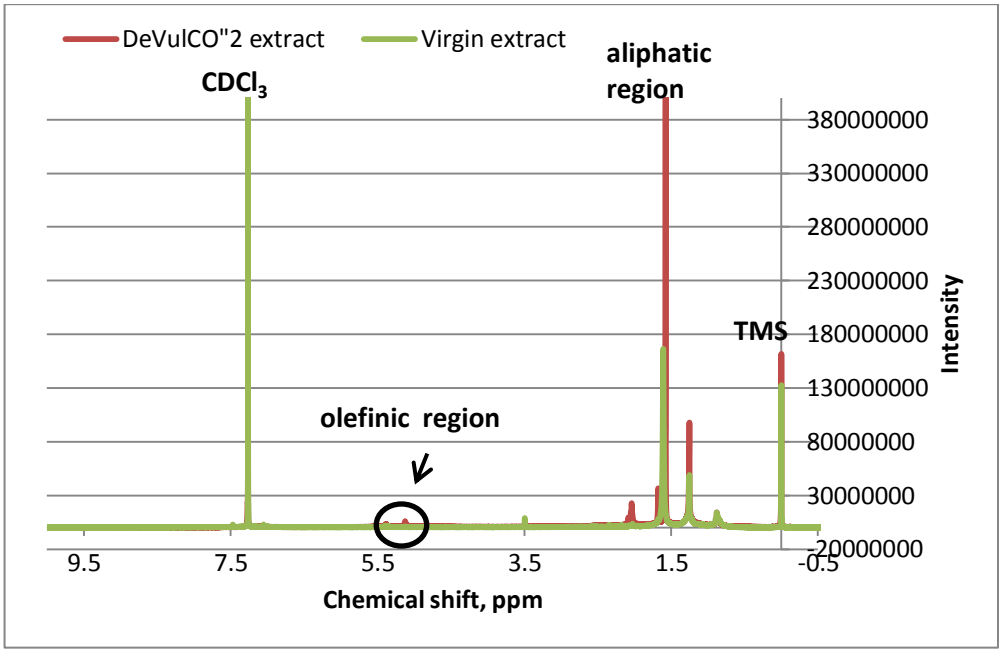


Fig. 5.5.6 ^{1}H-NMR spectra of Virgin and DeVulCO"2 extracts for closed-loop tyre materials

To compare to virgin material, the aliphatic region of the de-vulcanised sample shows well resolved peaks at around 1.68 ppm and 2.04 ppm that can be assigned to the methyl and methylene protons in the NR, BR and SBR rubbers. In addition, there is a clear difference in the strength of the signals between these samples in the olefinic region of the spectrum as illustrated in Fig. 5.5.7 and Fig. 5.5.8. This is particularly important as it can be potentially used to optimise the processing conditions and chemistry of the de-vulcanisation process. For example by comparing the olefinic region of the spectra of samples de-vulcanised under different conditions (such samples were not available).

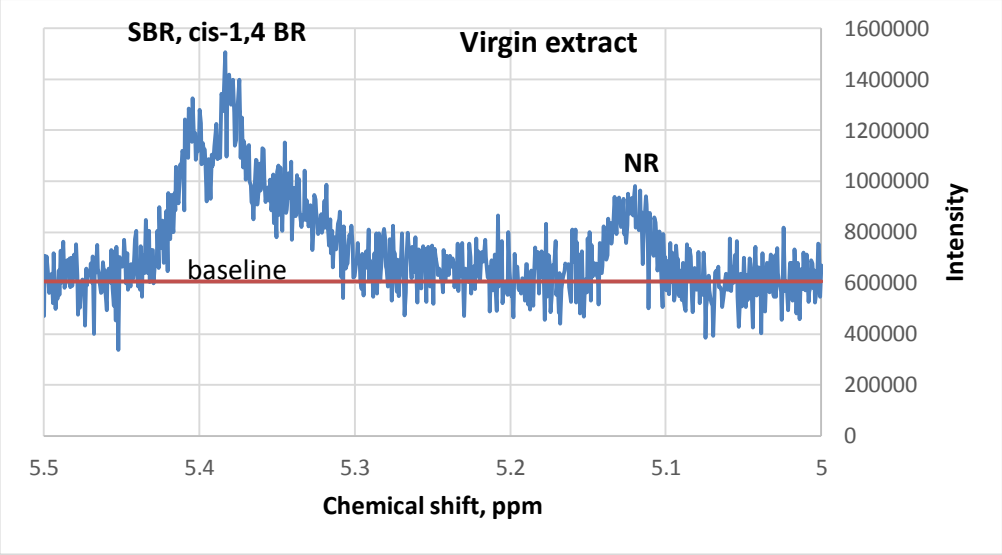


Fig. 5.5.7 Olefinic region of ^{1}H-NMR spectrum of virgin extract

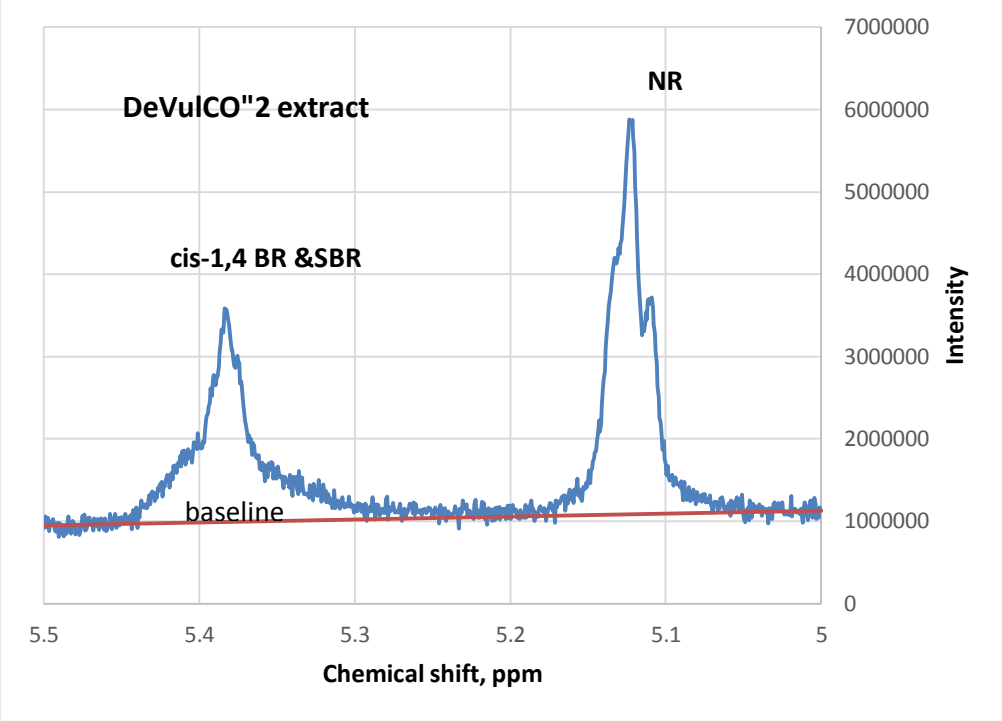


Fig. 5.5.8 Olefinic region of ^{1}H-NMR spectrum of DeVulCO"2 extract

To establish that the de-vulcanisation process worked equally well for all rubber components of the blend, the ratio between the two peak areas (NR and BR) for each material was determined and compared.

Due to the complexity of the peaks' shape and the weak signals in the case of the virgin extract (Fig. 5.5.), the area under the peaks was analysed manually, using the spectral data (intensity and frequency) imported to Microsoft excel. As with the analysis carried out on the swollen closed-loop tyre samples to find the width of the peak (H%), the frequencies in Hz were first converted to the

chemical shift in ppm. As illustrated in Fig. 5.5.7 and Fig. 5.5.8, a suitable baseline was then selected for each sample and the sum corrected for the baseline intensities, over the same range of chemical shifts (5.05-5.2 ppm for NR peak and 5.2-5.5 for BR peak) for both samples, provided the peak areas. In the case of the virgin extract (Fig. 5.5.7), the baseline was a straight line, close to the signals. However, the baseline for the DeVulCO"2 extract (Fig. 5.5.8) was sloping and this was taken into account when correcting to the baseline signal intensities.

The ratio of the NR to BR peak areas for both samples was then determined using equation 5.7 and gave the following results: **0.16 for virgin extract and 1.18 for De-VulCO"2**.

$$\frac{NR}{BR}ratio = \frac{\sum_{5.05ppm}^{5.2ppm} corrected\ for\ baseline\ intensities\ of\ NR\ peak}{\sum_{5.2ppm}^{5.5ppm} corrected\ for\ baseline\ intensities\ of\ BR\ peak} \qquad (\mathbf{5.7})$$

While the weak signals in the olefinic region of the virgin extract indicate some chain/ cross-link scission reactions during processing (e.g. oxidation), well resolved signals in the same region of the DeVulCO"2 sample are indicative of the effect of de-vulcanisation. If the effect of de-vulcanisation was the same for all rubber components of the blend, the ratio of the peak areas would stay the same after de-vulcanisation. The change in the peak areas ratio between the two samples (virgin and DeVulCO"2 extracts) indicated the difference in the efficiency of the de-vulcanisation process in relation to the individual rubber components of the tyre material (e.g NR and BR). The calculated results suggested a better de-vulcanisation efficiency of the NR component that is the major component of the tyre formulation (Table 1, Chapter 2) than BR.

This can be explained by the difference in the de-vulcanisation mechanism and the types of cross-links formed in these two rubbers. Studies carried out by Chapman and Johnson[190], highlighted the difference in the cross-linking mechanism at and above 150ºC in NR as compared to BR and SBR, resulting in a lower proportion of monosulphidic and higher proportion of carbon-carbon cross-links in the latter. This can be explained by temperature related free radical reactions that involve less zinc-accelerated species and lead to the formation of carbon-carbon cross-links between vinyl groups. As carbon-carbon bonds are stronger than C-$(S)_n$-C bonds, it would be expected to observe a lower degree of de-vulcanisation in BR and SBR rubber components of the tyre material compared to NR.

To sum up, the swollen state ^{1}H-NMR spectroscopy has been successfully applied in this study to characterise the width of the olefinic peak of closed-loop tyre materials that contain different amount of de-vulcanisate. The width of the olefinic peak appeared to increase with DeVulCO"2 loading. In addition, a linear correlation has been observed between the peak width parameter (H%) and the maximum torque, indicating an increase in the total level of cross-linking following the addition and increase in the de-vulcanised material. A good agreement in the results has also been observed between H% and the volume fraction of swollen rubber (except for 30% blend).

Moreover, a tool to measure the efficiency of the de-vulcanisation process has been devised based upon a comparison of the peak areas in the olefinic region of rubber extracts. Results obtained indicate the possibility of developing a technique that allows analysis of the efficiency of the de-vulcanisation process of the individual rubber components of the blend. The ^{1}H-NMR spectroscopy proved to be a way of analysing de-vulcanised material in crumb form, in terms of overcoming problems associated with material handling and reliability of the results.

5.6 Mechanical testing

The mechanical properties of the closed-loop tyre blends were analysed and compared to those for the virgin and de-vulcanised material. The relationship between the key mechanical properties of a rubber vulcanisate and its cross-link density parameter have been explained in section 1 (Introduction to vulcanisation and network structure) of Chapter 3. As the cross-link density increases, the modulus and hardness of the vulcanised rubber also increase as the rubber network becomes more elastic and less hysteretic. The schematic diagram (Fig. 3.2, Chapter 3), demonstrates a more complex behaviour for tensile and tear strength which tends to pass through the maximum at a particular level of cross-link density.

Hence, rubber materials have an optimum cross-link density range for practical use. The cross-link density level must be high enough to prevent failure by viscous flow but low enough to avoid brittle fracture.

Apart from the cross-link density level, the types of cross-links formed during the vulcanisation process (e.g. poly-, di-, monosulphidic, Fig. 3.6, Chapter 3) also have a significant effect on the mechanical properties of a rubber product. As explained earlier, poly- and disulphidic cross-links are associated with improved strength properties, whereas monosulphidic cross-links tend to improve the heat resistance of rubber (Fig. 3.8, Chapter 3). In this section the main mechanical properties of closed-loop tyre materials have been discussed and compared to the other network structure related parameters (e.g. volume fraction of rubber in swollen vulcanisate, maximum torque, peak broadness parameter H%). The composition of the closed-loop tyre materials discussed in this section were set-out in detail in Table 4.1 of Chapter 4 (Experimental work).

Hardness

The hardness of three round samples for each closed-loop tyre material were determined using the procedure described in section 4.7 (Mechanical testing) of Chapter 4. The results of the hardness test have been presented in Table 5.6.1.

Table 5.6.1 Results of hardness test for closed-loop tyre materials

Compound type	Virgin	5% blend	10% blend	15% blend	20% blend	25% blend	30% blend	100% DeVulCO"2
Hardness, IRHD								
Sample 1	69	66	66	67	69	71	70	72
Sample 2	69	65	66	67	71	71	70	73
Sample 3	69	64	66	67	70	71	70	74
Average	**69**	**65**	**66**	**67**	**70**	**71**	**70**	**73**
Standard deviation	±0	±1	±0	±0	±1	±0	±0	±1

A hardness measurement is a simple way of obtaining a measure of the elastic modulus of rubber material that is related to CRD. The hardness of the closed-loop tyre blends containing different amounts of DeVulCO"2 (Table 5.6.1) appeared to decrease slightly at low levels of addition (5 to 10%) and reach a value comparable to the virgin material value with increased loadings (20 to 30%). On the other hand, the value of hardness for the de-vulcanisate appeared to be slightly higher than for virgin material. To sum up, a slight variation (less than 6%) can be observed in the hardness of the closed-loop tyre materials with a partial or full replacement of virgin material by DeVulCO"2.

An extensive review of the properties of waste tyre rubber carried out by Ramarad et al[175] highlighted a general increase in hardness of rubber blends containing GTR or RTR. This was attributed to the filler-like effect of GTR or a similar effect from the remaining cross-links of RTR. Studies[47], based on the competitor to DeVulCO"2 de-vulcanisaton technology, the De-Link de-vulcanisation process, reported an increase, decrease or unchanged value of hardness when de-vulcanised tyre material was blended with the corresponding virgin compound. These changes were linked to the type of the virgin material and de-vulcanisate.

Compression set

The compression set is an important property of a rubber material as it investigates the long term effect of an applied stress or strain and is important for high performance rubber products such as tyres.

Three samples from each rubber compound were prepared and tested in accordance with the procedure explained in section 4.7 (Mechanical testing) of Chapter 4. At the end of the testing period (7 days at 120ºC), the samples were re-measured and their original and final dimensions were used to determine the compression set value, using equation 4.4 (Chapter 4). The results (mean values) of the compression set for the closed-loop tyre materials are presented in Table 5.6.2 and Fig. 5.6.1.

Table 5.6.2 Results of compression set test (7 days @ 120°C) for closed-loop tyre materials

Compound type	Virgin	5% blend	10% blend	15% blend	20% blend	25% blend	30% blend	100% DeVul-CO"2
Compression set results, %	96.9	98.1	88.9	88.3	84.3	84.4	83.9	81.0
Standard deviation	±0.43	±2.35	±1.59	±1.00	±0.68	±1.64	±0.37	±2.51

The results of the compression set (Table 5.6.2) showed improvements of up to 16.4% for this important property after addition of DeVulCO"2, with the best results achieved with a full replacement of the virgin material. The observed trend is in line with the competitor de-vulcanisation De-Link technology, where improvements of up to 9.3% were achieved in the SBR blend containing 30% of de-vulcanised material[47]. On the other hand, the results of a similar NR-based blend were difficult to compare due to the high value (6.9) of standard deviation.

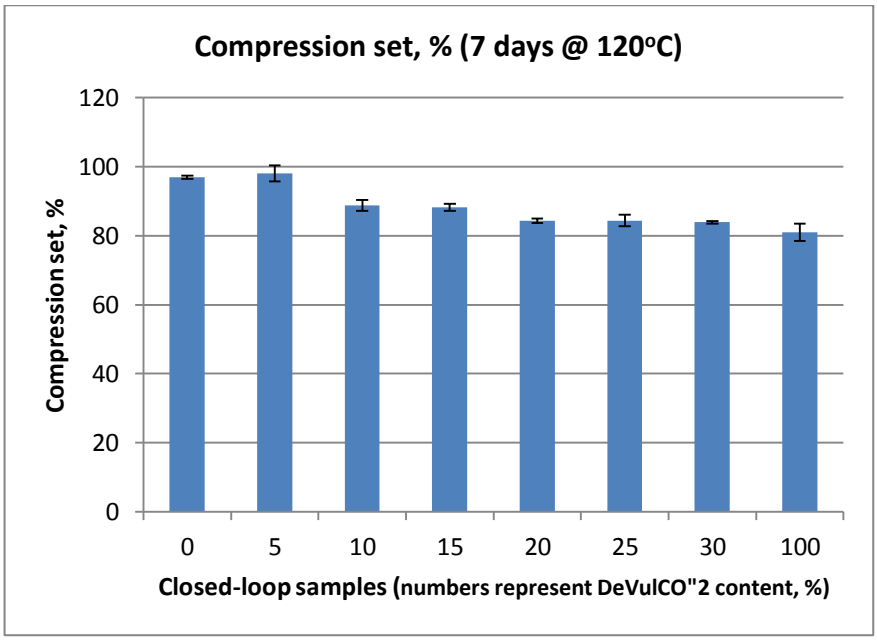


Fig. 5.6.1 Results of the compression set test for the closed-loop tyre materials

Tensile test

Tensile stress/strain measurements provide a guide to the quality of the rubber as well as demonstrating how a rubber product may behave under tension. The tensile properties of the closed-loop tyre materials were determined following the procedure described in section 4.7 (Mechanical testing) of Chapter 4. Five samples from each rubber compound were tested and any samples that did not break within the central (narrow) portion of the dumbbell sample were rejected. The QMat software was then employed to calculate the values of the tensile strength and

elongation at break for all closed-loop tyre materials. The results (mean values) of the tensile test have been presented in Table 5.6.3 and Fig. 5.6.2.

Table 5.6.3 Results of tensile test for closed-loop tyre materials

Compound type	Virgin	5% blend	10% blend	15% blend	20% blend	25% blend	30% blend	100% DeVul-CO"2
Tensile strength, MPa Standard deviation	10.1 ±0.95	10.5 ±0.94	11.5 ±0.97	13.0 ±1.02	13.3 ±0.31	13.5 ±0.60	14.4 ±0.29	10.5 ±0.37
Elongation at break, % Standard deviation	381 ±39.7	354 ±37.1	367 ±29.0	399 ±19.2	386 ±9.47	363 ±8.74	357 ±5.38	283 ±8.03

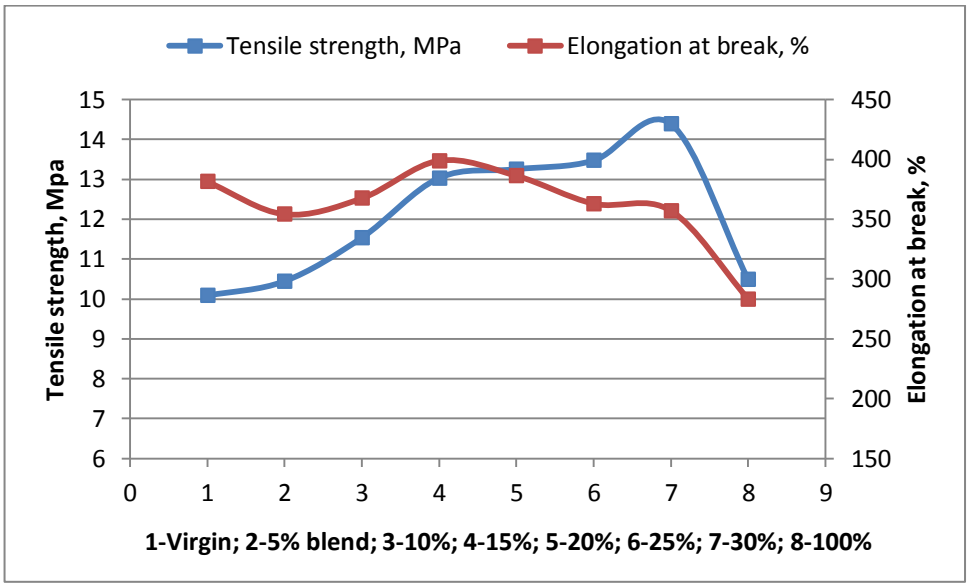


Fig. 5.6.2 Comparative results of tensile strength and elongation at break for closed-loop tyre materials

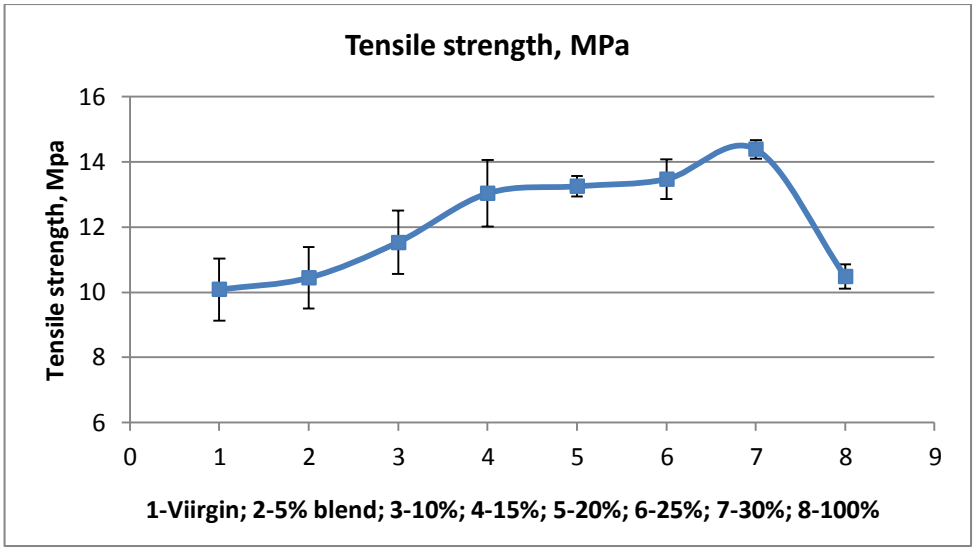


Fig. 5.6.3 Tensile strength results for closed-loop tyre materials

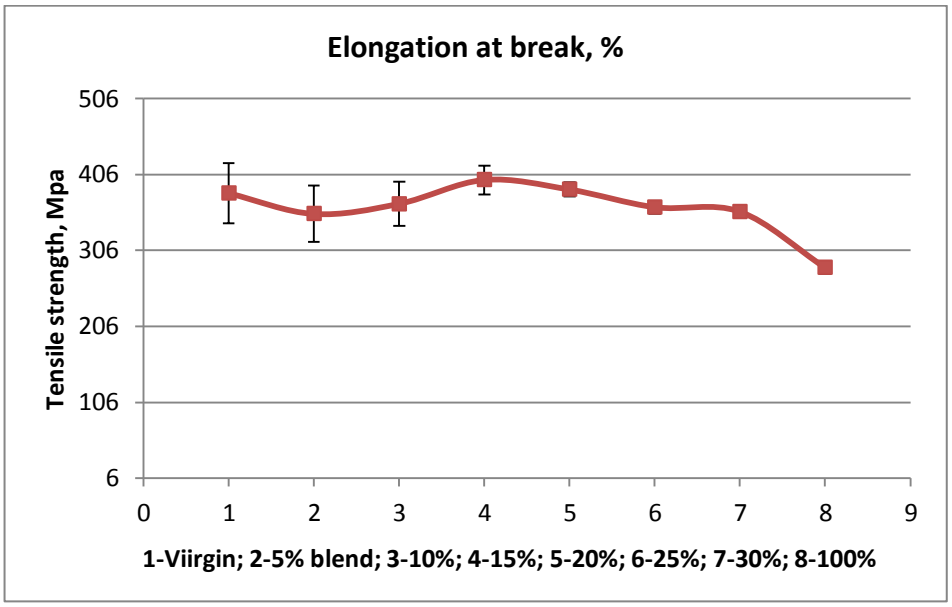


Fig. 5.6.4 Elongation at break results for closed-loop tyre materials

The general effect of adding GTR or RTR to the virgin material has been summarised by Ramarad et al[175] and is illustrated in Fig. 5.6.5.

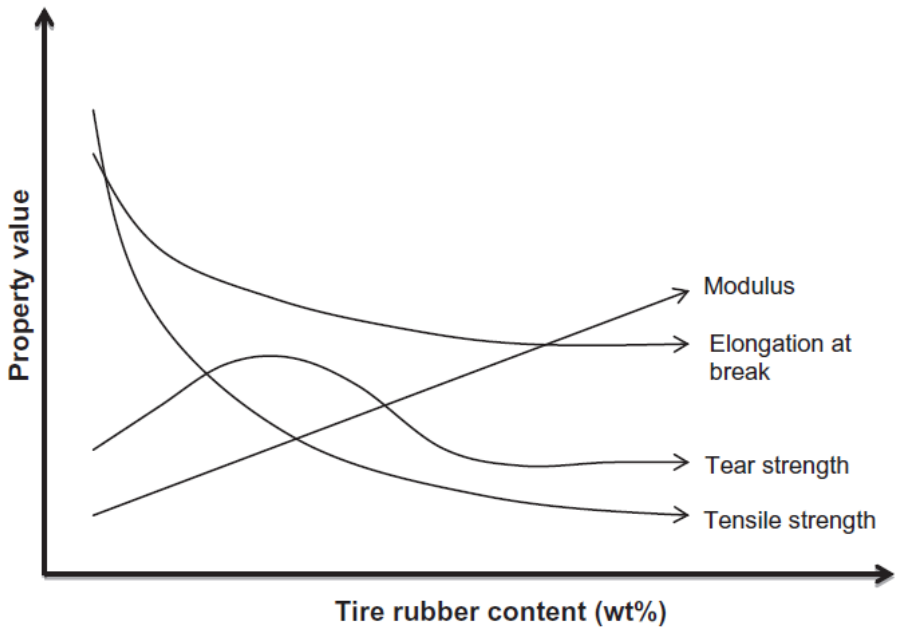


Fig.5.6.5 Change in common properties of blends containing ground and recycled tyre waste

As illustrated in Fig. 5.6.5 a reduction in values of elongation at break and tensile strength is generally observed with the addition of ground or recycled tyre rubber into a virgin NR-based compound. This was attributed to the remaining cross-links in the GRT or RTR phase of the continuous rubber blend matrix acting as stress concentration points, leading to reduction in these properties. Moreover, a study[32] focused on evaluating different waste tyre de-vulcanisation technologies, also reported a general reduction in tensile strength and elongation at break for general use tyre compounds containing de-vulcanised material. In addition, these studies reported a significant deterioration in tensile properties with increased amounts of de-vulcanisate.

In contrast, the property performance results of this study compare favourably to the existing recycling/de-vulcanisation technologies, indicating the great potential for this novel de-vulcanisation technology. As evident from Fig. 5.6.2, the addition of DeVulCO”2 appears to improve the tensile properties of the closed-loop tyre blends and show an increase in tensile strength with increased loadings of de-vulcanised material (e.g. 30% blend shows 43% increase as compared to the virgin sample). Moreover, the tensile strength of the de-vulcanised material (Fig. 5.6.3) is comparable to virgin material. It is noteworthy that the tensile strength of the virgin tyre compound is lower than expected for this type of material and that this has been verified by an independent testing laboratory. As illustrated in Fig. 5.6.4, the elongation at break does not appear to be significantly influenced by the addition of de-vulcanised material and the results for the 30% blend are still within the range of the virgin material. However, a significant drop in elongation at break can be observed in the case of pure de-vulcanisate (by approx. 25%) compared to virgin material.

Most importantly, the tensile test results have demonstrated that up to 20% of DeVulCO”2 can be

added to virgin material without any deterioration of these important parameters. This can be attributed to the improved efficiency of the DeVulCO"2 technology in comparison with competitor technologies.

The values of tensile strength were compared to the corresponding values of the volume fraction of swollen samples and the maximum torque results (Fig. 5.6.6 and Fig. 5.6.7).

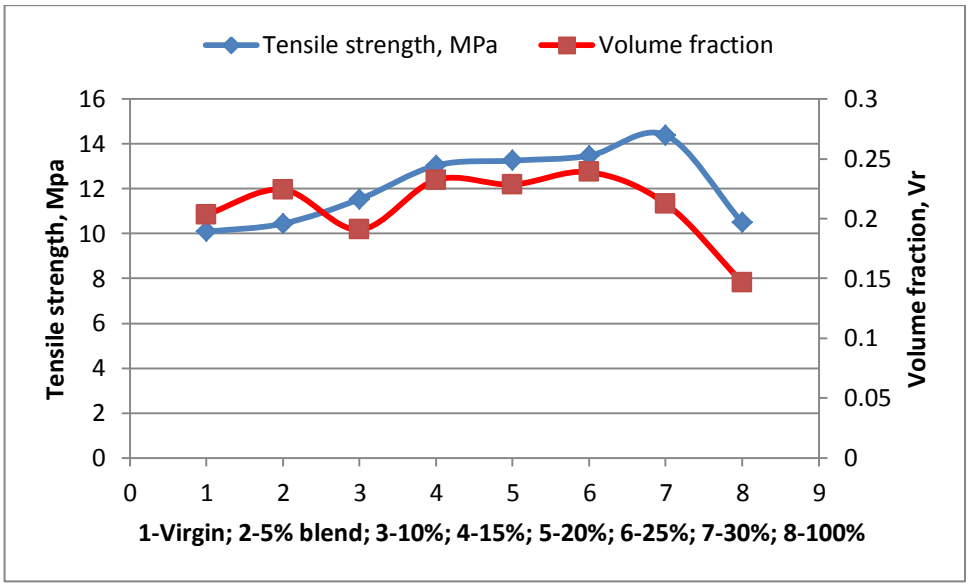


Fig. 5.6.6 Tensile strength and volume fraction results for closed-loop tyre materials

The volume fraction results appear to be in a good agreement with the tensile strength results (except for 10% blend), generally showing an increase in tensile strength with increase in V_r.

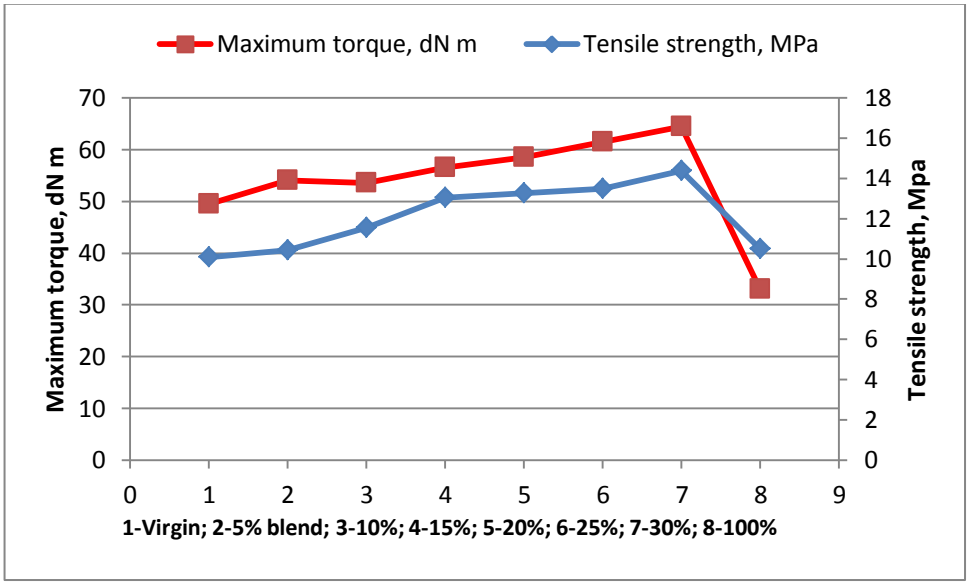


Fig. 5.6.7 Maximum torque and tensile strength results for closed-loop tyre materials

This is further supported by an observed agreement between tensile strength values and the

results of the maximum torque (Fig. 5.6.7) which is indicative of the total level of cross-linking. Therefore, increases in the total level of cross-links following additions of DeVulCO”2 seem to lead to an increase in tensile strength.

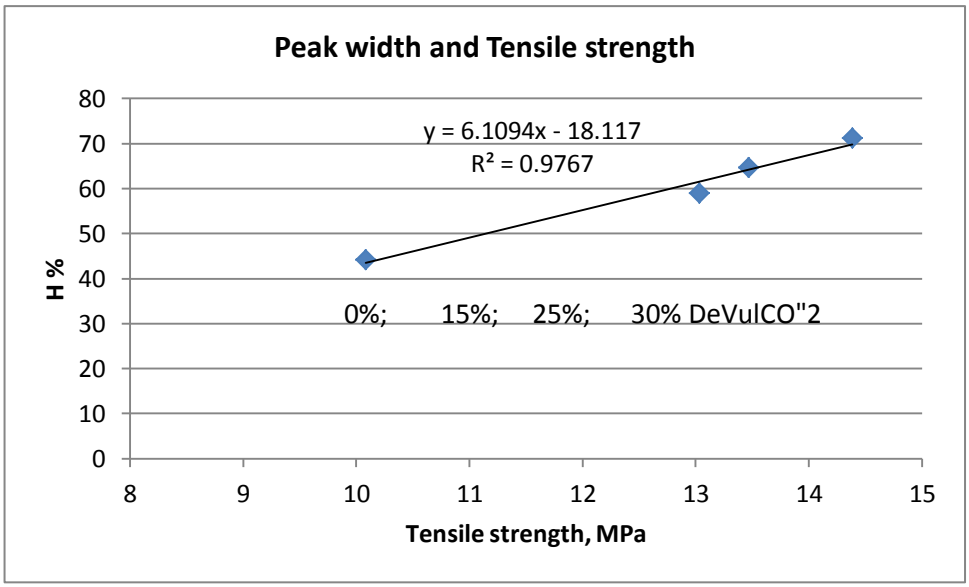


Fig. 5.6.8 Correlation between the peak width and tensile strength for the closed-loop tyre materials

Furthermore, as evident from Fig. 5.6.8 a correlation appears to exist between the width of the olefinic peak (H%) and the tensile strength of the closed-loop tyre materials, indicating that an increase in tensile strength can be associated with an increase in cross-link density.

Tear strength

Tear strength is one of the fundamental properties of a rubber product and is an important safety consideration in tyre materials. However, this property is usually adversely affected by the inclusion of recycled or de-vulcanised material[32,47,175].

Five samples from each closed-loop tyre compound were prepared and tested in accordance with the procedure outlined in section 4.7 (Mechanical testing) of Chapter 4. As explained, a trouser type test piece was selected for this work as it is not sensitive to the length of the cut. In addition, the results obtained on a trouser test piece can easily be related to the fundamental tear properties (e.g. tear strength) and are less sensitive to modulus effects observed with other type of test pieces (e.g. crescent). Furthermore, the rate of tear propagation can be directly related to the rate of grip separation.

The tear strength of the closed-loop tyre materials (mean value of 5 samples for each material) was determined as the median force to thickness ratio using QMat software. The results of the tear test are presented in Table 5.6.4 and Fig. 5.6.8.

Table 5.6.4 Results of tear test for closed-loop tyre materials

Compound type	Virgin	5% blend	10% blend	15% blend	20% blend	25% blend	30% blend	100% DeVul-CO"2
Tear strength, N mm-1 Standard deviation	24.5 ±5.85	19.7 ±4.95	17.8 ±4.70	17.8 ±5.35	15.0 ±1.60	13.8 ±2.65	14.9 ±1.17	6.20 ±0.29

It is evident from Table 5.6.4 that the tear strength of closed-loop tyre blends and pure de-vulcanisate is less than that of virgin material. However, as illustrated in Fig. 5.6. 9 the value of tear strength for blends up to 15% is still within a range of virgin material. A reduction in tear strength of carbon-black filled NR blends containing recycled/de-vulcanised material has been attributed to a poor adhesion between the virgin matrix and de-vulcanisate[175].

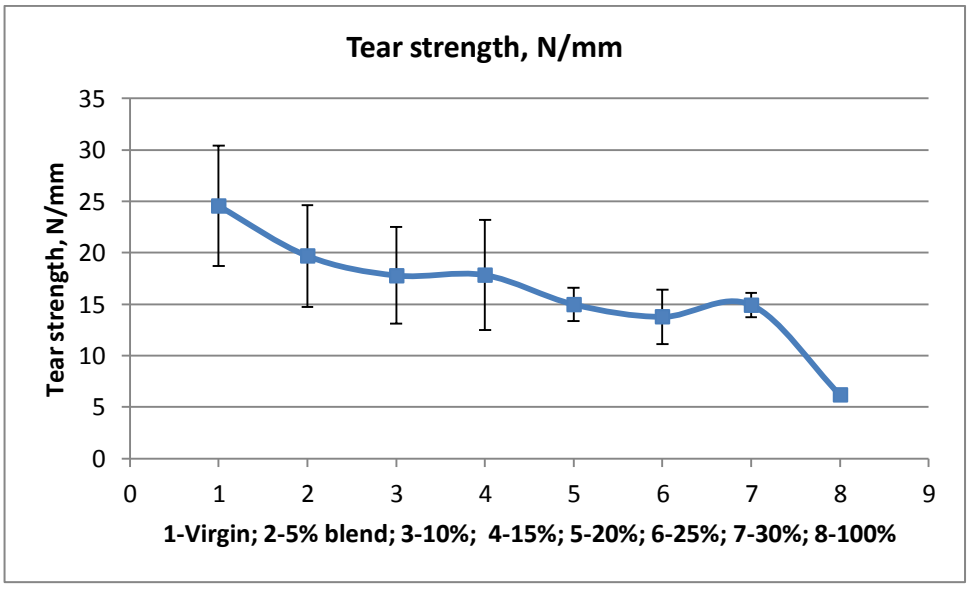


Fig. 5.6.9 Tear strength results for closed-loop tyre materials

The tear strength of black-filled NR vulcanisates has been related[157] to a useful range of cross-link densities and the types of cross-links. In addition, the type of elastomer and carbon black filler also influence the tear behaviour of rubber vulcanisates.

Three main types of tear related failure in rubbers have been outlined by Samsuri et al[160] namely steady (smooth), stick-slip and knotty tearing. Knotty tearing is often associated with strain-crystallising in reinforced elastomers, when the crack does not propagate continuously, but tends to deviate sideways, almost at 90^0 to the intended path. The reason for this type of behaviour has been attributed to the development of strength anisotropy around the tip of the tear[164] , leading to

the tear splitting along the direction of molecular orientation in the highly-oriented regions of local anisotropy around the tip of the tear[160]. The difference in tear related failure in closed-loop tyre materials is evident in Fig. 5.6.10 to Fig. 5.6.13. A typical knotty tearing behaviour can be observed in the virgin compound (with the crack propagation at 90^0 to the cut direction in the test piece, Fig. 5.6.10) which changes in the cases of pure de-vulcanisate (Fig.5.6.11) and blends (Fig. 5.6.12 and Fig. 5.6.13). The path of the crack propagation in the blends appears to be much longer with a lower angle in the cut direction as compared to pure de-vulcanisate.

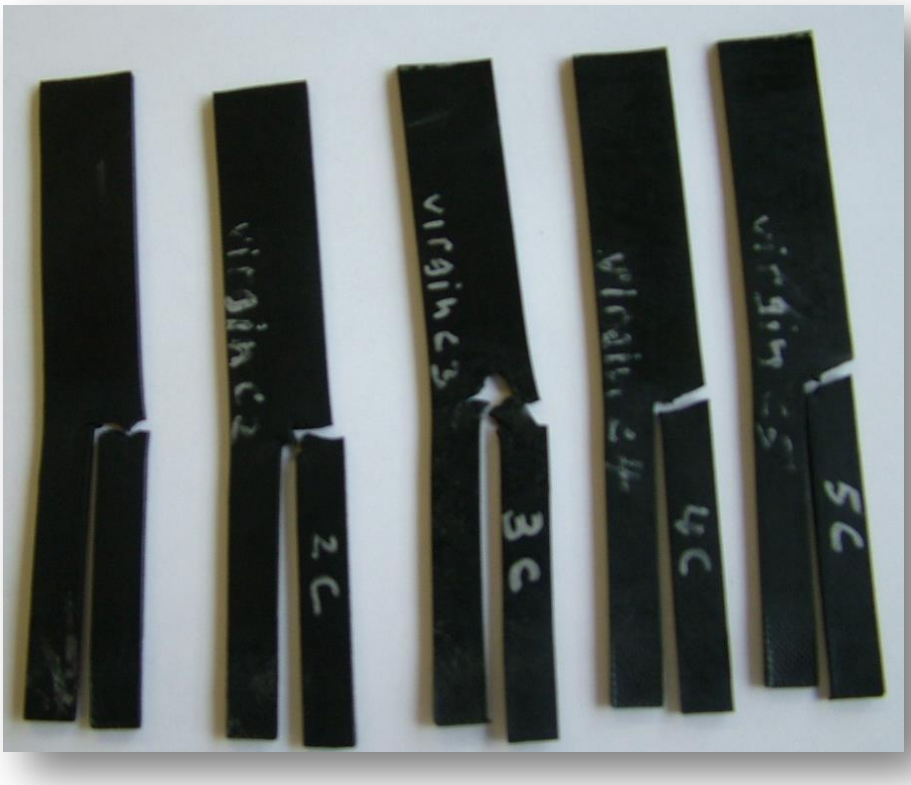


Fig. 5.6.10 Virgin closed-loop-tyre samples after tear test

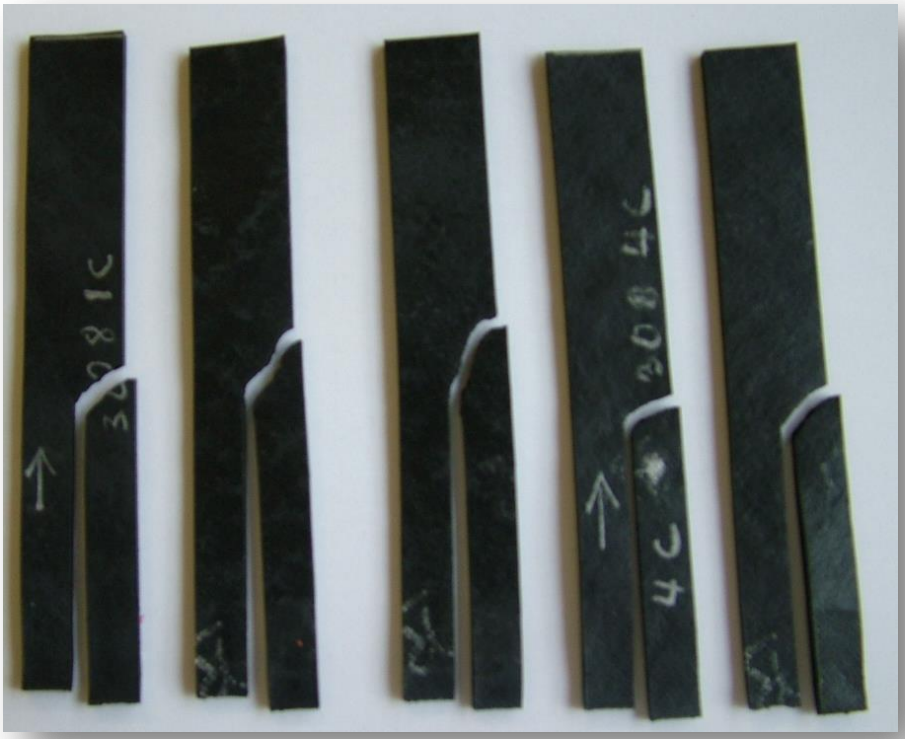


Fig. 5.6.11 DeVulCO"2 closed-loop samples after tear test

Fig. 5.6.12 25% blend closed-loop tyre samples after tear test

Fig. 5.6.13 30% blend closed-loop tyre samples after tear test

The difference in the tear behaviour for the closed-loop vulcanisate can be associated with differences in their cross-link density (Fig. 5.6.14 and Fig.5.6.15) and the types of cross-links formed on re-vulcanisation. The work seems to indicate that the tear strength is inversely proportional to the cross-link density of the blends. However, detailed fracture analysis would be required to explain the complexity of the observed fracture behaviour of the samples.

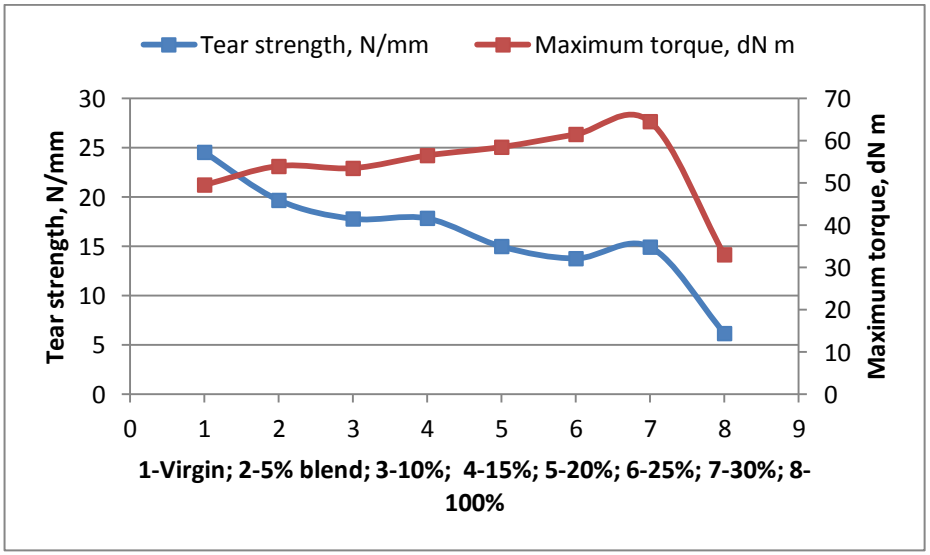


Fig. 5.6.14 Results of tear strength and maximum torque for closed-loop tyre materials

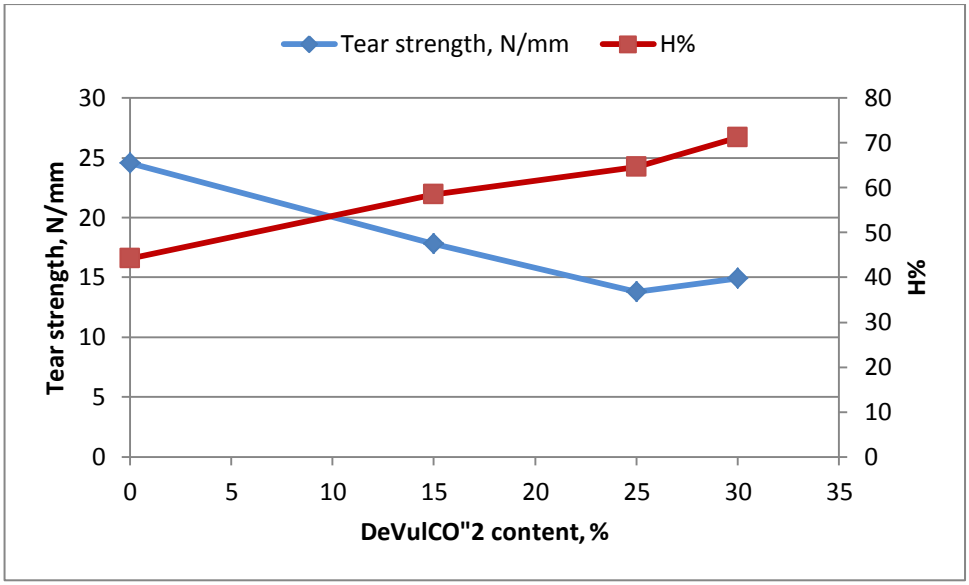


Fig. 5.6.15 Comparison of tear strength and H% for selected closed-loop materials

To sum up:

- The hardness of the samples is indicative of the modulus of rubber and tends to increase with the inclusion of recycled rubber. This was the case with samples having a higher level of de-vulcanised material (20% and above). Lower amounts (up to 15%) of de-vulcanised material led to reduced hardness.
- Compression set results (7 days @ 120^{o}C) were greatly improved by loading de-vulcanised material, with the 30% blend showing a 13 % improvement against the virgin material.
- The tensile strengths results of the de-vulcanised materials were comparable to virgin material and blends and showed increases in tensile strength as a result of loading of de-vulcanised material (e.g. 30% blend showed 43% increase against the virgin sample) whereas competitor technologies tend to decrease tensile strength.
- In comparison to virgin material, elongation at break slightly varied for the blends but significantly dropped in the case of de-vulcanised material (by approx. 25%).
- Tear strength results for blends up to 15% were comparable to the virgin material but reduced with higher loadings of DeVulCO”2. Comparison of tear strength and the results of M_H and H% indicated a reduction in this property with increasing cross-link density.

Chapter 6: Conclusions

An extensive literature review of well-established and emerging de-vulcanisation techniques identified *mechano-chemical DeVulCO"2 technology* as the most promising and environmentally sound rubber recovery method. It has been proven on a laboratory scale and is being trialled for commercialisation with the potential for development in high end applications, including new tyres. The lack of a suitable practical and reliable technique to evaluate the effectiveness of the de-vulcanisation process led to a comprehensive review of existing characterisation methods to identify a way of evaluating the closed-loop tyre compounds produced during commercial trials by the new DeVulCO"2 technology. Due to the nature of the work and hence, limited availability of de-vulcanised materials, EPDM-based automotive strip compounds and NR-based clothing tape compounds were also used in some tests.

A practical way to characterise de-vulcanised and re-vulcanised rubber materials and blends with virgin material was established. This work showed that parameters, which are simple to obtain and easy to understand, can be successfully used to indicate the efficiency of the de-vulcanisation process and hence, to assist during R&D stages and to maintain quality control. Moreover, these parameters may be acquired from tests that are commonly used in the rubber industry (Mooney viscosity, Mooney relaxation, curing). Good correlation was evident between these parameters and the network characterisation parameter (V_r) obtained from the swelling measurements that are known to be a reliable guide but are more time consuming to perform. In this work, the Mooney relaxation test was successfully extended to characterise *de-vulcanised* compounds (automotive strip and clothing tape). In addition, the swollen-state ^{1}H-NMR technique was successfully applied to characterise *de-vulcanised and re-vulcanised* closed-loop tyre materials. A new tool to measure the efficiency of the de-vulcanisation process has been devised, based on a comparison of the peak areas in the olefinic region of rubber extracts analysed by the liquid ^{1}H-NMR technique. This technique is capable of characterising the different components of a blend (e.g. NR, BR) and is suitable for carbon black filled compounds used in tyres. The results of this work have confirmed the strong potential of the DeVulCO"2 technology and indicate that up to 20% of de-vulcanisate (at least twice the amount offered by the existing reclaim or surface modification technologies) can be blended with virgin tyre material without significant deterioration of the key performance properties.

The main conclusions on the usefulness of the characterisation techniques that were employed in this work are set out in more detail below:

Mooney viscosity and Mooney relaxation

Mooney viscosity has been reported to indicate the efficiency of de-vulcanisation and this has been assessed using the closed-loop tyre materials, automotive weather strip EPDM-based materials and clothing tape NR-based materials. Mooney viscosity is easy to determine and is a characteristic of viscoelastic behaviour of unvulcanised rubber that can be related to the residual rubber network.

The Mooney viscosity of the closed-loop tyre blends showed similar results and were within the

range of the virgin material. This could be attributed to the dominant role of the virgin material within the composition of the blends or the use of additives known to reduce viscosity (e.g NR) during blending. However, the Mooney viscosity of the pure de-vulcanisate was high, indicating partial de-vulcanisation and the need for blending with virgin rubber to improve its quality and processability. On the other hand, the Mooney viscosities of the automotive weather strip blends and clothing tape blends were higher than for the corresponding virgin material. Furthermore the increased loading of de-vulcanised material in the blends led to increased viscosity that could be attributed to the restriction of flow caused by partially cross-linked crumb.

As the value of Mooney viscosity can be significantly influenced by processing conditions and additives, the Mooney relaxation test has been employed in this study to obtain additional information on the elastic component of de-vulcanised materials and blends. This novel approach involved evaluation of "non-standard" relaxation parameters to determine their potential to describe the elastic component of the material as a means for evaluating the de-vulcanisation process.

The main conclusions of this evaluation are presented below:

- Constant k has a high linear correlation with Mooney Viscosity and is therefore a characteristic of viscoelastic behaviour.
- Elasticity parameter, (α +1) is easier to interpret than α.
- Linear correlation exists between the Mooney relaxation parameters α and $M_{ret.30s}$ for both products, EPDM and NR.
- $M_{ret.30s}$ can potentially be used instead of the rate of relaxation as the more reliable, easier to determine and understand characterisation parameter.
- All main relaxation parameters for both products, EPDM and NR were in good agreement, showing increase in elasticity with addition and increase in de-vulcanisate that can be related to the remaining cross-links in de-vulcanised material and blends.
- Hence, the Mooney relaxation test offers potential as a more accurate evaluation of the de-vulcanisation process than Mooney viscosity as it provides information on the elastic component of un-vulcanised material.
- Mooney relaxation data can provide a useful addition to the Mooney viscosity results and can be related to the other characterisation parameters (e.g. V_r, H%) and mechanical properties.

Curing characteristics

The curing characteristics of de-vulcanised closed-loop tyre materials, automotive weather strip EPDM-based materials and clothing tape NR-based materials have been compared alongside their beneficial contribution to the efficiency of the de-vulcanisation process using the oscillating disc rheometer Monsanto 100.

The following conclusions were drawn from the curing characteristics results:

Minimum torque, M_L

- Minimum torque relates to the stiffness and viscosity of un-vulcanised rubber. In general, the minimum torque progressively increased with the addition of de-vulcanised material.
- The rate of relaxation showed a better sensitivity to the changes in minimum torque than Mooney viscosity and hence, may provide a better indication of de-vulcanisation efficiency.

Maximum torque, M_H

- As the de-vulcanised material is already cross-linked to some extent, the maximum torque, M_H can provide a more relevant measure of the total cross-linking.
- M_H for the closed-loop tyre blends and clothing tape blends increased continuously with increasing DeVulCO"2 content, indicating an increase in the total level of cross-linking. However, the opposite trend was observed with the automotive weather strip blends, where M_H decreased with increased DeVulCO"2 content.

Torque rise, M_H-M_L

- The torque rise relates to the formation of new cross-links. The torque rise, increased with the initial addition of de-vulcanised material for both, the closed-loop tyre blend and NR-based clothing tape blend. However, it did not change significantly on further addition.
- The torque rise reduced in the case of the automotive weather strip compounds.

Scorch time, t_{s2}

- Scorch time is an important parameter for processing safety. Scorch time significantly increased for the 100% de-vulcanised closed-loop tyre compound. However, the scorch times of the blends were lower than for the virgin compound.
- Scorch time also decreased in the case of the clothing tape blends.
- For both materials, increased loading of de-vulcanised material resulted in progressive decreases in the scorch time of the blends.
- In practical applications, de-vulcanised material is going to be used in blends and hence, further adjustments to the de-vulcanisation/re-vulcanisation process may be required.
- On the upside, excellent results were observed in the case of the automotive weather strip blends. There was no reduction in the scorch time with 15% loading and higher loadings led to an increase in the scorch time.

Maximum cure rate

- The maximum cure rate increased following the initial addition of de-vulcanised material for all three compounds.
- Increased loadings of DeVulCO"2 led to a further increase in the maximum cure rate except for EPDM blends, where a decrease in the maximum cure rate was observed at higher loadings.

- The maximum cure rate of 100% de-vulcanised closed-loop tyre compound was approximately 40 times lower than that for virgin material.

Cure rate index

- The cure rate index relates to the speed of vulcanisation. Similar to the trend observed with the maximum cure rate, the cure rate index increased with the initial addition of de-vulcanisate for all three materials. This could be beneficial to production efficiency (reduced vulcanisation time).
- Increased loadings of DeVulCO"2 led to further increase in the cure rate index until a maximum value (between 15% and 25% loading, depending on the material) was achieved. Further increases in de-vulcanisate, led to a decrease in the cure rate index.
- However, the cure rate index of the pure closed-loop tyre de-vulcanisate was 5 times less than the corresponding virgin compound, highlighting the need for blending for practical use.

Swelling measurements

The following conclusions have been drawn from the swelling measurements results:

Amount of sol

- The values of sol in closed-loop tyre blends were similar to one another and to the virgin material, except for the 10% and 25% blends which could have been affected by processing conditions during blending.
- The amount of sol for un-vulcanised DeVulCO"2 was significantly higher than for the blends and the virgin material, indicating cross-link breaking caused by de-vulcanisation.
- The amount of sol for un-vulcanised DeVulCO"2 significantly decreased on re-vulcanisation and became comparable to the values of blends and virgin material, indicating cross-linking taking place on re-vulcanisation.

Volume fraction of rubber in swollen vulcanisate

- The values of the volume fraction in closed-loop tyre blends were similar to one another and to the virgin material, except for 10% and 30% blends that were slightly lower.
- The value of volume fraction for un-vulcanised DeVulCO"2 was lower than for the blends and virgin material, indicating network reduction following de-vulcanisation. The value of volume fraction for re-vulcanised DeVulCO"2 was comparable to the value of virgin compound and the blends.
- A similar trend in the results has been evident between the volume fraction and Mooney viscosity for the closed-loop blends. In addition, some similarities have been observed between torque rise and volume fraction (except for 30% blend).

FTIR spectroscopy

The following conclusions were drawn from the FTIR results:

- FTIR-ATR requires minimal sample preparation and proved useful in studying the consistency and polymer composition of incoming recycled material.
- Although some differences were observed between the spectrum of the original and de-vulcanised rubber crumb, they did not appear to be significant enough to guide optimisation of the de-vulcanisation process.
- The acetone extracts of the closed-loop tyre compounds containing DeVulCO"2 showed an emerged peak at around 1540 cm^{-1}. However, quantitative analysis of the peak area did not establish any useful outcomes that can be related to the de-vulcanisation study.
- The residue of the closed-loop tyre compounds did not have enough resolved peaks in the spectra to be useful.

NMR spectroscopy

Swollen state ^{1}H-NMR spectroscopy has been successfully applied in this study to characterise the width of the olefinic peak of de-vulcanised closed-loop tyre materials containing different amount of de-vulcanisate (gel). The peak width parameter (H%) increases as the peak broadens, corresponding to an increase in cross-link density and hence, can be used to assess the efficiency of de-vulcanisation.

The following conclusions have been drawn from the NMR results:

- The width of the olefinic peak appeared to increase with DeVulCO"2 loading.
- In addition, a linear correlation has been observed between the peak width parameter (H%) and the maximum torque, indicating an increase in the total level of cross-linking following the addition and increase of de-vulcanised material.
- A good agreement in the results has also been observed between H% and the volume fraction of swollen rubber (except for 30% blend).
- A new tool to measure the efficiency of the de-vulcanisation process has been devised based on a comparison of the peak areas in the olefinic region of rubber extracts (sol). The calculated results suggest a better de-vulcanisation efficiency of the NR component (the major component of the tyre formulation) than BR. These results indicate the possibility of developing a technique that allows evaluation of the de-vulcanisation efficiency for the individual rubber components of the blend (e.g. NR, BR).
- The ^{1}H-NMR spectroscopy proved to be a way of analysing de-vulcanised material in crumb form by overcoming problems associated with material handling and reliability of the results.

Mechanical testing

The mechanical properties of the closed-loop tyre blends were analysed and compared to those for

the virgin and de-vulcanised material.

The following conclusions have been drawn from the mechanical tests:

- The hardness of the samples is indicative of the modulus of rubber and tends to increase with the inclusion of recycled rubber. This was the case with samples including a higher level of de-vulcanised material (20% and above). Lower amounts (up to 15%) of de-vulcanised material led to reduced hardness.
- Compression set results (7 days @ 120^{o}C) were greatly improved by loading de-vulcanised material, with the 30% blend showing a 13 % improvement against the virgin material.
- The tensile strengths results of the de-vulcanised materials were comparable to virgin material and blends and showed increases in tensile strength as a result of loading of de-vulcanised material (e.g. 30% blend showed 43% increase against the virgin sample) whereas alternative de-vulcanising technologies tend to decrease tensile strength.
- Correlation between M_H, V_r, H% and tensile strength were observed, indicating an increase in tensile strength with an increase in cross-link density.
- In comparison to virgin material, elongation at break slightly varied for the blends but significantly dropped in the case of de-vulcanised material (by approx. 25%).
- Tear strength results for blends up to 15% were comparable to the virgin material but reduced with higher loadings of DeVulCO”2. Comparison of tear strength and the results of M_H and H% indicated a reduction in this property with increasing cross-link density.

A summary of observed relationships between the main characterisation parameters and mechanical properties for de-vulcanised rubber compounds and blends are presented in Table 6.1.

Table 6.1 Summary of observed relationships between the main characterisation parameters and mechanical properties for de-vulcanised rubber compounds and blends

Characterisation technique	**Material state**	**Main characterisation parameters**	**Correlations**
Mooney Viscosity	De-vulcanised	MV	*MV* and *k* *MV* and V_r
Mooney Relaxation	De-vulcanised	k, a, (a+1), $M_{ret.30s}$	*(a+1)* & $M_{ret.30s}$ *a* and M_L
Curing parameters		M_L,M_H, (M_H-M_L), Maximum cure rate	M_L and *a* (M_H-M_L) and V_r M_H and *H%* M_H and *tensile & tear strength*
Equilibrium swelling	De-vulcanised and re-vulcanised	V_r	V_r and *MV* V_r and (M_H-M_L) (V_r and Mooney relaxation not investigated) V_r and *H%* V_r and *tensile strength*
^{1}H-NMR spectroscopy -swollen state ^{1}H-NMR -liquid state ^{1}H-NMR	 Re-vulcanised (gel) De-vulcanised crumb (sol)	 H% olefinic peak area	*H%* and M_H *H%* and V_r *H%* and *tensile & tear strength*

Chapter 7: Recommendations for further work

This work demonstrated the potential for using Mooney relaxation parameters to supplement Mooney viscosity results to indicate the efficiency of de-vulcanisation of unvulcanised compounds and blends. For example, the results of the Mooney relaxation parameter "*a"* for the automotive strip compounds showed a better agreement with the curing parameter M_L that relates to elastic behaviour of rubber, than the Mooney viscosity results. However, further work will be required to establish the full potential of the Mooney relaxation test by using the same material (e.g. closed-loop tyre compound) to determine all characterisation parameters and relate them to mechanical properties. As the availability of the materials used in this work was based on industrial trials, consistent use of the same material was not always possible.

Valuable conclusions have been drawn from the results of the curing characteristics. However, the exact explanation of the observed behaviour could not be established due to a lack of information on the vulcanisation/de-vulcanisation chemicals used. For example, the complex effect of the DeVulCO"2 on the cure rate index observed in this work in closed-loop tyre blends could be related to the rates of two competing reactions: the formation of new cross-links and the loss of cross-links during vulcanisation through inefficient cross-link shortening reactions. However, without detailed knowledge of the ingredients used in the virgin closed-loop compound formulation and de-vulcanisation chemicals, the chemistry and mechanism behind these changes cannot be explained. Therefore, more knowledge of materials and de-vulcanisation details are required to interpret the results and correlations observed, and gain a better understanding of the de-vulcanisation mechanism of this technology as a whole.

^{1}H- NMR spectroscopy proved to be a useful tool in characterising de-vulcanised and re-vulcanised closed-loop tyre materials. It would be beneficial to extend this work to characterise automotive strip and clothing tape compounds in order to compare results with the closed-loop materials.
The new tool to measure the efficiency of the de-vulcanisation process, devised in this work and based on a comparison of the peak areas in the olefinic region of rubber extracts (sol) needs further proving by using rubber materials, produced at different de-vulcanisation conditions and/or chemistry.

The results of mechanical properties have confirmed the great potential of materials, de-vulcanised by the DeVulCO"2 technology. However, in order to be used in high performance applications such as tyres, further tests on actual products will be required to establish the optimum proportion of de-vulcanisate in the blend.

Tear strength is an important characteristic of rubber products and is particularly relevant to tyres. The tearing behaviour of rubber compounds used in this work can be further investigated to improve this important property. Fracture analysis of the tearing surfaces of the re-vulcanised samples and consideration of the tearing energy could provide the background information needed

to explain the tear behaviour observed in closed-loop compounds.

It has been shown in this work that the network structure of rubber has a significant influence on the mechanical properties of rubber materials and therefore, requires characterisation. Existing characterisation techniques were further developed in this work to successfully characterise the network of de-vulcanised and re-vulcanised rubber compounds and blends. The characterisation parameters, identified by this study, can be further used to construct a correlation with selected mechanical properties of vulcanisates (particularly when complimented by a calibration plot of modulus against cross-link density of samples vulcanised to different degree) and hence, to guide the R&D stages of the de-vulcanisation process.

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Appendix 1: “Typical” truck tyre formulation

Table 1: Composition of the “typical” truck tyre compounds*

Ingredients	Example 1 (pphr)	Example 2 (pphr)
Natural rubber (SMR 10 CV)	70	80
Butadiene rubber	30	20
Carbon black (N234)	50	53
Eneflex oil	0	4
Zinc oxide	3.5	5
Stearic acid	2.4	2
Anti-degradant (6PPD)	2.4	2
Antioxidant (TMQ)	1.5	0
Wax	1.0	0
Sulphur	1.2	1.8
Accelerator (TBBS)	1.1	1.0

*WRAP Project Report: Recycling of Tyre Rubber Into New Rubber Products Through Efficient De-vulcanisation. 2007 Jul. (Waste and Resources Action Programme (WRAP)). Report No.: Project code: TyR3-012.

Appendix 2: "Typical" automotive weather strip formulation

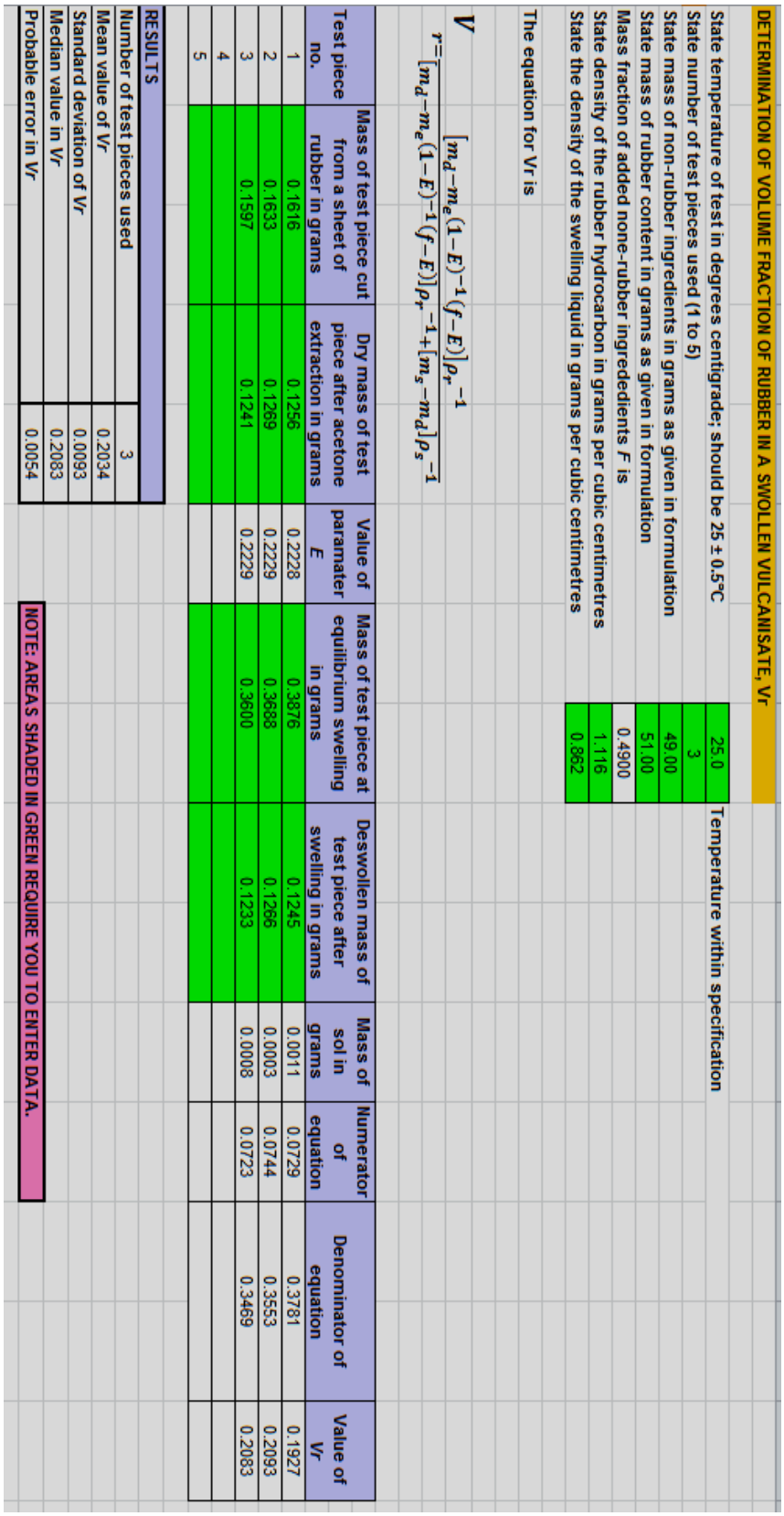
Table 1: Composition of the "typical" automotive weather strip compound[**]

Ingredients	**Amount (pphr)**
EPDM	100
Paraffinic oil	45
Carbon black (N550)	105
Stearic acid	1
Zinc oxide	5
DEG	3
Sulphur	1.5
MBT	1.5
TMTD	0.5
TBBS	0.5
ZDBC	1.5
DTDM	1.5
Stabiliser (Struktol^{R} HM 97)	2

[**] Larsen L.C. The reduction of iridescence bloom in elastomeric weather-stripping application. In:18th National Rubber Conference 2007. Eastern Cape, South Africa; March 9, 2007.

Appendix 3: Swelling measurement results

Table 1: Calculations of sol portion and volume fraction of swollen virgin closed-loop tyre compound



DETERMINATION OF VOLUME FRACTION OF RUBBER IN A SWOLLEN VULCANISATE, Vr

State temperature of test in degrees centigrade; should be 25 ± 0.5°C	25.0	Temperature within specification
State number of test pieces used (1 to 5)	3	
State mass of non-rubber ingredients in grams as given in formulation	49.00	
State mass of rubber content in grams as given in formulation	51.00	
Mass fraction of added none-rubber ingredients *F* is	0.4900	
State density of the rubber hydrocarbon in grams per cubic centimetres	1.116	
State the density of the swelling liquid in grams per cubic centimetres	0.862	

The equation for Vr is

$$V_r = \frac{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1}}{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1} + [m_s - m_d]\rho_s^{-1}}$$

Test piece no.	Mass of test piece cut from a sheet of rubber in grams	Dry mass of test piece after acetone extraction in grams	Value of paramater *E*	Mass of test piece at equilibrium swelling in grams	Deswollen mass of test piece after swelling in grams	Mass of sol in grams	Numerator of equation	Denominator of equation	Value of *Vr*
1	0.1616	0.1256	0.2228	0.3876	0.1245	0.0011	0.0729	0.3781	0.1927
2	0.1633	0.1269	0.2229	0.3688	0.1266	0.0003	0.0744	0.3553	0.2093
3	0.1597	0.1241	0.2229	0.3600	0.1233	0.0008	0.0723	0.3469	0.2083
4									
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RESULTS	
Number of test pieces used	3
Mean value of *Vr*	0.2034
Standard deviation of *Vr*	0.0093
Median value in *Vr*	0.2083
Probable error in *Vr*	0.0054

NOTE: AREAS SHADED IN GREEN REQUIRE YOU TO ENTER DATA.

Table 2: Calculations of sol portion and volume fraction of swollen 5% blend closed-loop tyre compound

DETERMINATION OF VOLUME FRACTION OF RUBBER IN A SWOLLEN VULCANISATE, Vr

State temperature of test in degrees centigrade; should be 25 ± 0.5°C	25.0	Temperature within specification
State number of test pieces used (1 to 5)	3	
State mass of non-rubber ingredients in grams as given in formulation	54.60	
State mass of rubber content in grams as given in formulation	46.40	
Mass fraction of added none-rubber ingredients *F* is	0.5406	
State density of the rubber hydrocarbon in grams per cubic centimetres	0.878	
State the density of the swelling liquid in grams per cubic centimetres	0.862	

The equation for Vr is

$$V_r = \frac{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1}}{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1} + [m_s - m_d]\rho_s^{-1}}$$

Test piece no.	Mass of test piece cut from a sheet of rubber in grams	Dry mass of test piece after acetone extraction in grams	Value of paramater *E*	Mass of test piece at equilibrium swelling in grams	Deswollen mass of test piece after swelling in grams	Mass of sol in grams	Numerator of equation	Denominator of equation	Value of *Vr*
1	0.1830	0.1436	0.2153	0.4291	0.1428	0.0008	0.0948	0.4269	0.2221
2	0.1709	0.1341	0.2153	0.3952	0.1334	0.0007	0.0886	0.3923	0.2258
3	0.1690	0.1326	0.2154	0.3901	0.1314	0.0012	0.0870	0.3871	0.2248
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RESULTS

Number of test pieces used	3
Mean value of *Vr*	0.2242
Standard deviation of *Vr*	0.0019
Median value in *Vr*	0.2248
Probable error in *Vr*	0.0011

NOTE: AREAS SHADED IN GREEN REQUIRE YOU TO ENTER DATA.

Table 3: Calculations of sol portion and volume fraction of swollen 10% blend closed-loop tyre compound

DETERMINATION OF VOLUME FRACTION OF RUBBER IN A SWOLLEN VULCANISATE, Vr

State temperature of test in degrees centigrade; should be 25 ± 0.5°C	25.0	Temperature within specification
State number of test pieces used (1 to 5)	3	
State mass of non-rubber ingredients in grams as given in formulation	51.90	
State mass of rubber content in grams as given in formulation	48.10	
Mass fraction of added none-rubber ingrededients *F* is	0.5190	
State density of the rubber hydrocarbon in grams per cubic centimetres	1.171	
State the density of the swelling liquid in grams per cubic centimetres	0.862	

The equation for Vr is

$$V_r = \frac{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1}}{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1} + [m_s - m_d]\rho_s^{-1}}$$

Test piece no.	Mass of test piece cut from a sheet of rubber in grams	Dry mass of test piece after acetone extraction in grams	Value of paramater *E*	Mass of test piece at equilibrium swelling in grams	Deswollen mass of test piece after swelling in grams	Mass of sol in grams	Numerator of equation	Denominator of equation	Value of *Vr*
1	0.1570	0.1233	0.2146	0.3568	0.1230	0.0003	0.0642	0.3355	0.1915
2	0.1527	0.1199	0.2148	0.3506	0.1197	0.0002	0.0626	0.3304	0.1894
3	0.1526	0.1198	0.2149	0.3481	0.1197	0.0001	0.0626	0.3276	0.1911
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RESULTS	
Number of test pieces used	3
Mean value of *Vr*	0.1907
Standard deviation of *Vr*	0.0012
Median value in *Vr*	0.1911
Probable error in *Vr*	0.0007

NOTE: AREAS SHADED IN GREEN REQUIRE YOU TO ENTER DATA.

Table 4: Calculations of sol portion and volume fraction of swollen 15% blend closed-loop tyre compound

DETERMINATION OF VOLUME FRACTION OF RUBBER IN A SWOLLEN VULCANISATE, Vr

State temperature of test in degrees centigrade; should be 25 ± 0.5°C	25.0	Temperature within specification
State number of test pieces used (1 to 5)	3	
State mass of non-rubber ingredients in grams as given in formulation	48.97	
State mass of rubber content in grams as given in formulation	51.03	
Mass fraction of added none-rubber ingrededients *F* is	0.4897	
State density of the rubber hydrocarbon in grams per cubic centimetres	1.008	
State the density of the swelling liquid in grams per cubic centimetres	0.862	

The equation for Vr is

$$V_r = \frac{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1}}{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1} + [m_s - m_d]\rho_s^{-1}}$$

Test piece no.	Mass of test piece cut from a sheet of rubber in grams	Dry mass of test piece after acetone extraction in grams	Value of paramater *E*	Mass of test piece at equilibrium swelling in grams	Deswollen mass of test piece after swelling in grams	Mass of sol in grams	Numerator of equation	Denominator of equation	Value of *Vr*
1	0.1507	0.1184	0.2143	0.3455	0.1188	-0.0004	0.0767	0.3397	0.2258
2	0.1512	0.1188	0.2143	0.3315	0.1181	0.0007	0.0759	0.3234	0.2345
3	0.1430	0.1123	0.2147	0.3117	0.1118	0.0005	0.0719	0.3038	0.2367
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RESULTS	
Number of test pieces used	3
Mean value of *Vr*	0.2323
Standard deviation of *Vr*	0.0058
Median value in *Vr*	0.2345
Probable error in *Vr*	0.0033

NOTE: AREAS SHADED IN GREEN REQUIRE YOU TO ENTER DATA.

Table 5: Calculations of sol portion and volume fraction of swollen 20% blend closed-loop tyre compound

DETERMINATION OF VOLUME FRACTION OF RUBBER IN A SWOLLEN VULCANISATE, Vr

State temperature of test in degrees centigrade; should be 25 ± 0.5°C	25.0	Temperature within specification
State number of test pieces used (1 to 5)	3	
State mass of non-rubber ingredients in grams as given in formulation	50.17	
State mass of rubber content in grams as given in formulation	49.83	
Mass fraction of added none-rubber ingrededients *F* is	0.5017	
State density of the rubber hydrocarbon in grams per cubic centimetres	1.032	
State the density of the swelling liquid in grams per cubic centimetres	0.862	

The equation for Vr is

$$V_r = \frac{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1}}{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1} + [m_s - m_d]\rho_s^{-1}}$$

Test piece no.	Mass of test piece cut from a sheet of rubber in grams	Dry mass of test piece after acetone extraction in grams	Value of paramater *E*	Mass of test piece at equilibrium swelling in grams	Deswollen mass of test piece after swelling in grams	Mass of sol in grams	Numerator of equation	Denominator of equation	Value of *Vr*
1	0.1625	0.1275	0.2154	0.3505	0.1267	0.0008	0.0777	0.3373	0.2303
2	0.1557	0.1221	0.2158	0.3405	0.1212	0.0009	0.0743	0.3287	0.2260
3	0.1503	0.1179	0.2156	0.3264	0.1174	0.0005	0.0721	0.3145	0.2292
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RESULTS	
Number of test pieces used	3
Mean value of *Vr*	0.2285
Standard deviation of *Vr*	0.0022
Median value in *Vr*	0.2292
Probable error in *Vr*	0.0013

NOTE: AREAS SHADED IN GREEN REQUIRE YOU TO ENTER DATA.

Table 6: Calculations of sol portion and volume fraction of swollen 25% blend closed-loop tyre compound

DETERMINATION OF VOLUME FRACTION OF RUBBER IN A SWOLLEN VULCANISATE, Vr

State temperature of test in degrees centigrade; should be 25 ± 0.5°C	25.0	Temperature within specification
State number of test pieces used (1 to 5)	3	
State mass of non-rubber ingredients in grams as given in formulation	49.90	
State mass of rubber content in grams as given in formulation	50.10	
Mass fraction of added none-rubber ingrededients *F* is	0.4990	
State density of the rubber hydrocarbon in grams per cubic centimetres	1.009	
State the density of the swelling liquid in grams per cubic centimetres	0.862	

The equation for Vr is

$$V_r = \frac{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1}}{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1} + [m_s - m_d]\rho_s^{-1}}$$

Test piece no.	Mass of test piece cut from a sheet of rubber in grams	Dry mass of test piece after acetone extraction in grams	Value of paramater *E*	Mass of test piece at equilibrium swelling in grams	Deswollen mass of test piece after swelling in grams	Mass of sol in grams	Numerator of equation	Denominator of equation	Value of *Vr*
1	0.1603	0.1280	0.2015	0.3439	0.1279	0.0001	0.0795	0.3301	0.2409
2	0.1672	0.1335	0.2016	0.3639	0.1332	0.0003	0.0827	0.3504	0.2361
3	0.1658	0.1324	0.2014	0.3561	0.1319	0.0005	0.0818	0.3419	0.2394
4									
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RESULTS	
Number of test pieces used	3
Mean value of *Vr*	0.2388
Standard deviation of *Vr*	0.0024
Median value in *Vr*	0.2394
Probable error in *Vr*	0.0014

NOTE: AREAS SHADED IN GREEN REQUIRE YOU TO ENTER DATA.

Table 7: Calculations of sol portion and volume fraction of swollen 30% blend closed-loop tyre compound

DETERMINATION OF VOLUME FRACTION OF RUBBER IN A SWOLLEN VULCANISATE, Vr

State temperature of test in degrees centigrade; should be 25 ± 0.5°C	25.0	Temperature within specification
State number of test pieces used (1 to 5)	3	
State mass of non-rubber ingredients in grams as given in formulation	47.67	
State mass of rubber content in grams as given in formulation	52.33	
Mass fraction of added none-rubber ingrededients *F* is	0.4767	
State density of the rubber hydrocarbon in grams per cubic centimetres	1.217	
State the density of the swelling liquid in grams per cubic centimetres	0.862	

The equation for Vr is

$$V_r = \frac{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1}}{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1} + [m_s - m_d]\rho_s^{-1}}$$

Test piece no.	Mass of test piece cut from a sheet of rubber in grams	Dry mass of test piece after acetone extraction in grams	Value of paramater *E*	Mass of test piece at equilibrium swelling in grams	Deswollen mass of test piece after swelling in grams	Mass of sol in grams	Numerator of equation	Denominator of equation	Value of *Vr*
1	0.1587	0.1274	0.1972	0.3461	0.1271	0.0003	0.0680	0.3221	0.2112
2	0.1589	0.1276	0.1970	0.3445	0.1270	0.0006	0.0679	0.3202	0.2119
3	0.1683	0.1351	0.1973	0.3601	0.1341	0.0010	0.0716	0.3338	0.2144
4									
5									

RESULTS	
Number of test pieces used	3
Mean value of *Vr*	0.2125
Standard deviation of *Vr*	0.0017
Median value in *Vr*	0.2119
Probable error in *Vr*	0.0010

NOTE: AREAS SHADED IN GREEN REQUIRE YOU TO ENTER DATA.

Table 8: Calculations of sol portion and volume fraction of swollen 100% DeVulCO"2 closed-loop tyre compound

DETERMINATION OF VOLUME FRACTION OF RUBBER IN A SWOLLEN VULCANISATE, Vr

State temperature of test in degrees centigrade; should be 25 ± 0.5°C	25.0	Temperature within specification
State number of test pieces used (1 to 5)	3	
State mass of non-rubber ingredients in grams as given in formulation	47.00	
State mass of rubber content in grams as given in formulation	53.00	
Mass fraction of added none-rubber ingredients *F* is	0.4700	
State density of the rubber hydrocarbon in grams per cubic centimetres	1.163	
State the density of the swelling liquid in grams per cubic centimetres	0.862	

The equation for Vr is

$$V_{r=}\frac{[m_d-m_e(1-E)^{-1}(f-E)]\rho_r^{-1}}{[m_d-m_e(1-E)^{-1}(f-E)]\rho_r^{-1}+[m_s-m_d]\rho_s^{-1}}$$

Test piece no.	Mass of test piece cut from a sheet of rubber in grams	Dry mass of test piece after acetone extraction in grams	Value of paramater *E*	Mass of test piece at equilibrium swelling in grams	Deswollen mass of test piece after swelling in grams	Mass of sol in grams	Numerator of equation	Denominator of equation	Value of *Vr*
1	0.1777	0.1585	0.1080	0.4298	0.1585		0.0810	0.3957	0.2047
2	0.2023	0.1805	0.1078	0.4921	0.1799	0.0006	0.0917	0.4539	0.2021
3	0.2000	0.1784	0.1080	0.4923	0.1782	0.0002	0.0910	0.4554	0.1998
4									
5									

RESULTS	
Number of test pieces used	3
Mean value of *Vr*	0.2022
Standard deviation of *Vr*	0.0024
Median value in *Vr*	0.2021
Probable error in *Vr*	0.0014

NOTE: AREAS SHADED IN GREEN REQUIRE YOU TO ENTER DATA.

Table 9: Calculations of sol portion and volume fraction of swollen un-vulcanised 100% DeVulCO"2 closed-loop tyre compound

DETERMINATION OF VOLUME FRACTION OF RUBBER IN A SWOLLEN VULCANISATE, Vr

State temperature of test in degrees centigrade; should be 25 ± 0.5°C	25.0	Temperature within specification
State number of test pieces used (1 to 5)	3	
State mass of non-rubber ingredients in grams as given in formulation	43.93	
State mass of rubber content in grams as given in formulation	56.07	
Mass fraction of added none-rubber ingrededients *F* is	0.4393	
State density of the rubber hydrocarbon in grams per cubic centimetres	1.087	
State the density of the swelling liquid in grams per cubic centimetres	0.862	

The equation for Vr is

$$V_r = \frac{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1}}{[m_d - m_e(1-E)^{-1}(f-E)]\rho_r^{-1} + [m_s - m_d]\rho_s^{-1}}$$

Test piece no.	Mass of test piece cut from a sheet of rubber in grams	Dry mass of test piece after acetone extraction in grams	Value of paramater *E*	Mass of test piece at equilibrium swelling in grams	Deswollen mass of test piece after swelling in grams	Mass of sol in grams	Numerator of equation	Denominator of equation	Value of *Vr*
1	0.1679	0.1469	0.1251	0.5234	0.1389	0.0080	0.0792	0.5253	0.1509
2	0.1645	0.1439	0.1252	0.4920	0.1307	0.0132	0.0727	0.4919	0.1478
3	0.1698	0.1486	0.1249	0.5241	0.1344	0.0142	0.0745	0.5266	0.1415
4									
5									

RESULTS	
Number of test pieces used	3
Mean value of *Vr*	0.1467
Standard deviation of *Vr*	0.0048
Median value in *Vr*	0.1478
Probable error in *Vr*	0.0028

NOTE: AREAS SHADED IN GREEN REQUIRE YOU TO ENTER DATA.